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STABILITY OF GLASS FIBER-PLASTIC COMPOSITES

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Abstract - Continued

on the individual components in the system and on samples of composites made of these components. It was found that the glass filaments are a reactive component and lose their strength rapidly on direct exposure to water at elevated temperatures. Magnesium is a particularly active component. It was also found that the silane coupling agent that is incorporated in standard commercial glass finishes is a possible reactive component.

It is recommended that research be conducted to find ways to stabilize the glass and glass fiber-epoxy composite structural materials against water degradation. A possible experimental research program was outlined for this purpose. It was emphasized that the most pronounced need is to establish a formulation and application procedure for a protective finish material. This material is a critical part of the structural system and should not be left as a proprietary, unregulated part of the system.

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I. INTRODUCTION

A. Objective

The purpose of this research is to determine the stages and nature of degradation of glass fiber-plastic composite systems under various environmental conditions. The information gained is to be directed towards the definition of conditions favorable to stability and retention of desirable mechanical properties.

B. Nature of the System and the Degradation Problem

Glass fiber-plastic composite materials are of several basic types. For a number of years a consumer product known as "fiber-glass" has been used in connection with building construction and automotive and marine applications. In this material, a mat or felt of glass fibers is laid over a form and impregnated with a plastic mixture, that when cured, produces the desired composite. In the application of these composite materials the loads are supported primarily by the matrix plastic, and the glass filaments serve to stiffen the matrix. Strengths are of the order of the strength of the matrix plastic material; the stiffness is somewhat enhanced by the incorporated glass.

A variety of filamentary materials are available with strengths appreciably higher than those obtainable in any of the homogeneous structural alloys used for missile or other critical design applications. Characteristic values are tabulated below. (1)* Each of these materials has a strength value approaching the order of one

*Numbers in parentheses refer to listings in BIBLIOGRAPHY.

TABLE I
PROPERTIES OF TYPICAL STRUCTURAL FILAMENTS

Filament	Strength (ksi)	Modulus (10 ⁶ psi)	Specific Gravity	Form
Boron	600	59	2.6	Continuous, polycrystalline deposit on tungsten wire
E-Glass	500	10.5	2.6	Continuous
Graphite	3,000	140	2.0	Continuous
Piano wire	600	30	7.8	Continuous
S-Glass	650	12.5	2.5	Continuous
Silicon Carbide	575	65	3.4	Whiskers, (~3cm)

million pounds per square inch, but fall into two categories based on available dimensions. These two categories lead naturally to two basic types of composite materials: short filament and continuous filament. The advanced composites that may be fabricated utilizing these new materials have strengths based primarily upon the load-carrying capabilities of the filaments. The matrix material provides or maintains integrity of the structure and serves to distribute loads between filaments and to other structural members of the overall system. Composite strength can be estimated as the linear result of the strengths of the individual materials in proportion to the amount present. Analysis shows that in the case of the short filament

composite, under optimum conditions of short-filament distribution, the effective strength contribution of the filament is one-half of its strength.

Continuous-filament composite materials have strength levels that are higher than those obtainable by any of the available aluminum structural alloys. Glass fiber-epoxy composite materials which are of direct importance to missile structural component design are in this category. Other types of composite materials may have strengths surpassing those available in any homogeneous structural alloys. The following table lists typical properties of advanced composite materials. (1)

TABLE II
PROPERTIES OF SELECTED STRUCTURAL COMPOSITES

Filament	Matrix	Strength (ksi)	Modulus (psi x 10 ⁶)
E-Glass	Epoxy	250	8
S-Glass	Epoxy	290	9.6
Graphite	Epoxy	210	12.5
Boron	Epoxy	210	32
Steel	Epoxy	425	21

The continuous-filament, glass fiber-epoxy composites have the additional advantage in that both the glass and the reactants for

the epoxy matrix are relatively inexpensive and readily available. Also, the technology for fabrication of a large variety of structural shapes is already established. Perhaps the most pronounced drawback in the use of such systems is the fact that the composites are degraded with respect to mechanical properties by simple, prolonged exposure to high humidity levels at relatively high storage temperatures. Gnapp conducted extensive investigations of the effects of these variables on strengths of rocket motor cases. (2). These are summarized in Figure 1. This degradation is, of course, intolerable in a structural member designed with near critical values as are employed in military components.

At the time this research was initiated, there was no clear definition of the locale or nature of the degradation process in the composite materials system. There were indications that the degradation may be the result of reactions with the polymer matrix, the glass filaments, or the development of some structural condition at the interface.

C. Constitution of Structural Glasses

A variety of structural glasses are used in continuous-filament composite materials. The S-glass is used principally for rocket and missile structural composites because of its exceptionally high strength. The structure of each is based on the silicon-oxygen, glassy structure as modified by the presence of other oxide components. Depending on the valence of the cation in the oxide, the addition of the oxide to the silicon dioxide can have its effect

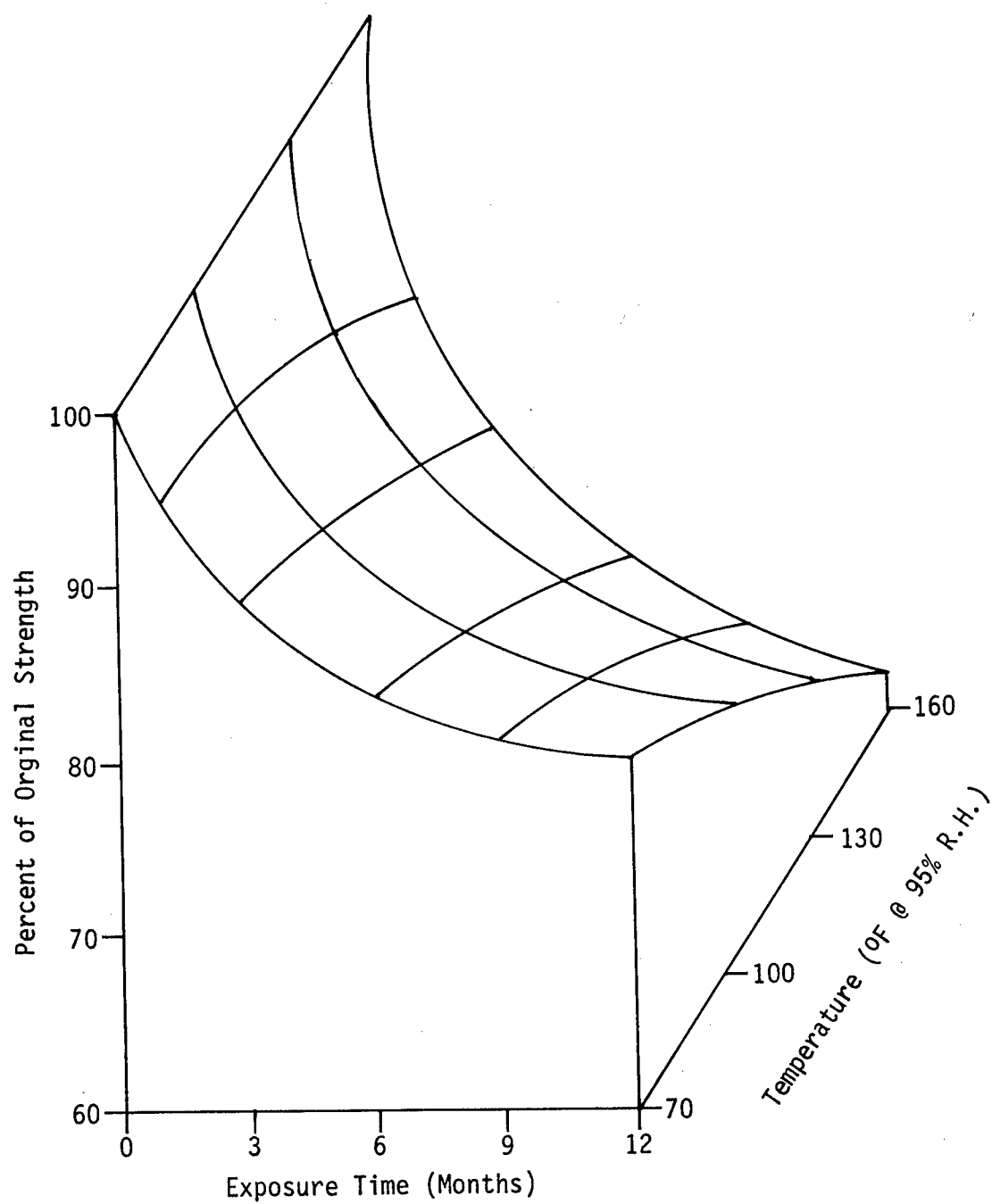


Figure 1. Effects of exposure time and temperature on the hydrostatic burst strength at 100°F of filament wound glass-epoxy pressure vessels. (2)

either on the structure of the continuing matrix or as an interstitial modifier. The scientific literature contains many reports of research relating to the heat treatment and modification of the structure of the glasses. (3-7).

To better understand the possible mechanism of water degradation of glass and the effects on phase separation within the glass as a result of thermal treatments to remove the coupling agent, a literature survey of the constitution of structural glasses was undertaken. Phase equilibrium relationships for both S-glass and E-glass were investigated.

1. S-Glass

The formation of S-glass is proprietary and differs between the two main sources (Owens-Corning and Ferro Corporation) from which samples were obtained for this research program. However, according to published work by Humphrey (8) of Owens-Corning, the approximate composition of S-glass (994) is 65% SiO_2 , 25% Al_2O_3 and 10% MgO . From the $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ diagram (9) in Figure 2, the composition of S-glass lies on the Alkemade line between SiO_2 and $2\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ (cordierite). Under equilibrium conditions, that is with total crystallization of phases, only the two phases, quartz and cordierite should be present in the relative amounts of 28.3% and 71.7%, respectively.

Considering only equilibrium solidification, the phase to nucleate initially would be mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). Solidification then proceeds to the boundary separating the primary phase fields of

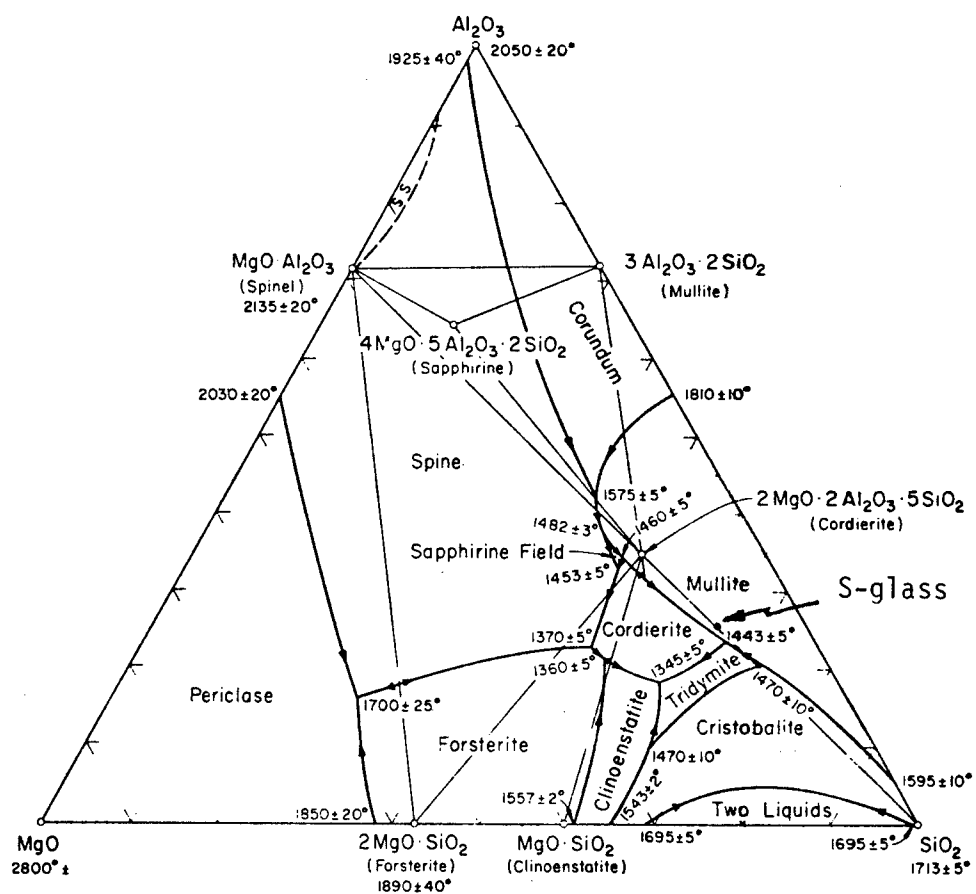
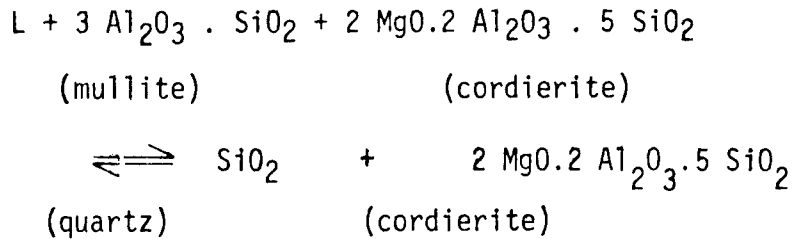


Figure 2. System MgO-Al₂O₃ - SiO₂ showing the approximate composition of S-glass.

mullite and cordierite. Along this boundary, positive crystallization of cordierite along with negative crystallization (peritectic type reaction) of mullite occurs until final solidification takes place at 1443°C by means of the peritectic reaction:



However, there is the possibility of some mullite being present in the final crystalline state, if equilibrium is not quite obtained during the final peritectic reaction.

Any slight variation in composition could also produce a third crystalline phase. Maintaining the SiO_2 and increasing the MgO would produce some clinoenstatite ($\text{MgO} \cdot \text{SiO}_2$). On the other hand, an increase in Al_2O_3 would cause mullite to form. In all likelihood, any variation in composition would also involve SiO_2 . It is thus assumed that the composition of S-glass varies essentially along the Alkemade with the only noticeable effect in constitution being a variation in the relative amounts of quartz and cordierite present on crystallization.

When non-equilibrium conditions exist, such as in the formation of a glass, the cooling rate is rapid, an amorphous and not a crystalline structure is obtained and the equilibrium amounts of the phases are not produced. It is also possible that one of the normal phases will not form. With rapid cooling it is doubtful that either mullite or clinoenstatite will form even with a slight change in

composition. It is assumed that rapid cooling during glass formation will result in an increase in SiO_2 and less cordierite than under equilibrium conditions. Under the right conditions of thermal treatments, separation of these phases within the glass by means of crystallization can occur. However, crystallization of cordierite does not occur below about 980°C (10-13). Any thermal treatment used in the preparation of S-glass fibers prior to incorporation into composites or prior to testing will be at a considerably lower temperature (on the order of 550°C). The results of various thermal treatments will be discussed later in this report.

2. E-Glass

E-glass is a calcium-magnesium-aluminoborosilicate containing trace amounts of alkali oxides. The approximate composition (8) is

52% SiO_2

18% CaO

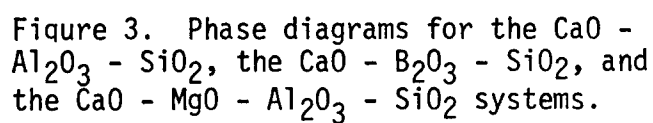
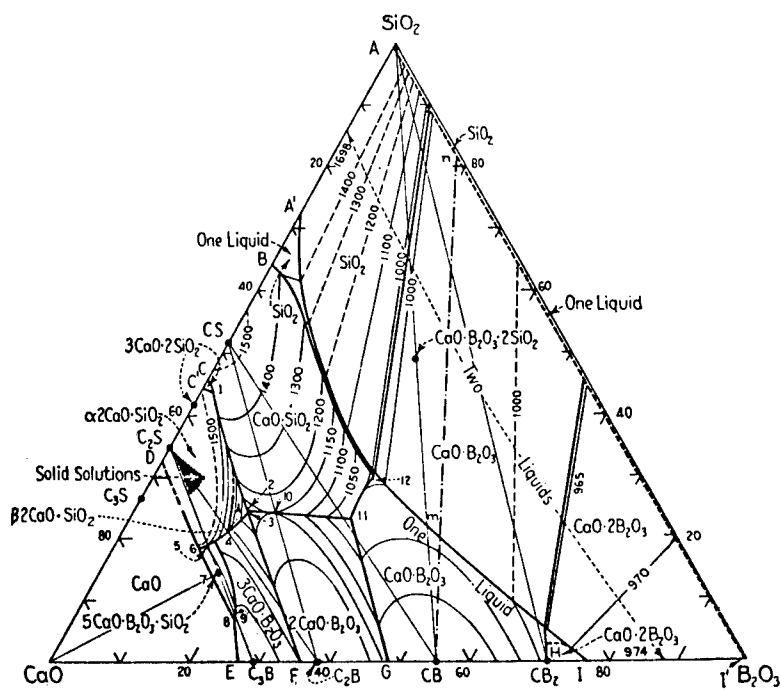
14% Al_2O_3

11% B_2O_3

4% MgO

1% Na_2O and K_2O

A search of the literature did not produce a diagram of phase equilibria for the four major components. Only separate diagrams (9), Figure 3, for the $\text{CaO-B}_2\text{O}_3\text{-SiO}_2$, $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ and $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-MgO}$ could be found. Thus, an indepth analysis of the crystalline phases which may be present under equilibrium conditions could not be made. It is felt, however, that four types of phases or



combinations of these types might be present. These four phases, without regard to their compositions, are:

1. quartz (SiO_2)
2. CaO.SiO_2
3. $\text{CaO.B}_2\text{O}_3$
4. $\text{CaO.MgO.Al}_2\text{O}_3.\text{SiO}_2$

The drawing temperature of E-glass is at least 500°F less than for S-glass (8). E-glass should not be as thermally stable as S-glass. Thus, crystallization may occur in E-glass at lower temperatures.

The glass filaments are manufactured by melting marbles in the composition that had been made in a prior stage of the process. In the case of one manufacturer, a supply of glass marbles in the S-glass composition was made more than ten years ago, and is expected to be adequate to supply future needs for military applications for at least ten years and possibly several decades. The marbles are melted and poured through a platinum manifold with as many openings as there are filaments in the roving that is produced. Typical numbers are 108, 216, etc. The glass is drawn from the bushing at a speed of approximately 30 miles per hour and is coated either by spraying or by contact with the surface of a wet roller. The liquid contains the various finishing agents to be incorporated on the surface, and a solution which evaporates away. In the case of S-glass, this finishing solution is non-aqueous and proprietary. The finish material has the purpose of holding the filaments together in the roving; of protecting the individual filaments from abrasion

damage that may occur during handling; of promoting wetting by the polymer that is to form the matrix; and should hopefully provide a protection against the effects of moisture and other chemical substances that may react with the glass and interfere with adhesion.

The diameters of the glass filaments are controlled primarily by the temperature of the melt and the rate of withdrawal from the manifold. There is a variation in diameters; the observed standard deviation is approximately one-tenth the mean diameter. The rate of cooling is so fast in the typical manufacturing process that there is not much time for the separation of phases in the system. If there is any tendency for phase separation because of the relative instability of the quenched structure, this may happen later as a result of heating during curing of the composite or during other heating stages that might be involved.

There was a significant episode in the chemistry of the glass-water system. Polywater was reported internationally as a new phase of water that was formed within the structural confines of quartz capillaries. Bascom found, however, that this was a complex silicate-carbonate formed with the reaction products of the glass-water reaction. (14)

During the past decade, a number of studies have been conducted of the reaction between water and glass or quartz, usually in a bulk form rather than in a fine, filamentary structure. In one experiment, however, relatively fine rods of glass were embedded in epoxy and polished to a high degree of surface finish perfection. The intensity of light lost by scattering along the length of the

filaments was measured precisely, and it was found that the effect of moisture is to increase the scattering and light loss. (15). The conclusion was that the matrix epoxy was being separated from the surface of the glass, either by a reaction with the glass or by the formation of a sub-microscopic phase at the interface.

The reactivity of epoxy materials with water is not believed to be of concern. They are permeable by water and water may apparently be incorporated in the epoxy phase with a resultant modification, usually enhancement of mechanical properties; but there is no apparent degradation or direct reaction.

In addition to the basic reactivity of the glass with water, it is observed that glassy materials are subject to stress corrosion. There are also reports of the effect of composition, especially with respect to substitutional cation radius on the corrosion susceptibility and stress-corrosion susceptibility of glasses. (16).

Figure 4 is a stereographic pair of pictures representing the structure of a section of the glass-epoxy system. This may be viewed to advantage in three dimensions, using either a stereographic viewer or by using the images with the help of a small piece of cardboard as a field divider between the left-hand and right-hand images. The silicon-oxygen phase segment is typical of crystalline quartz with hydroxyl groups at the surface, and the epoxy molecule shown was originally bi-functional but has reacted at one of the -OH groups at the surface of the hydrated quartz. The unreacted epoxide functional group is shown at the top of the molecule. The inter-atomic dimensions are correct, based upon reported measurements in the literature. The

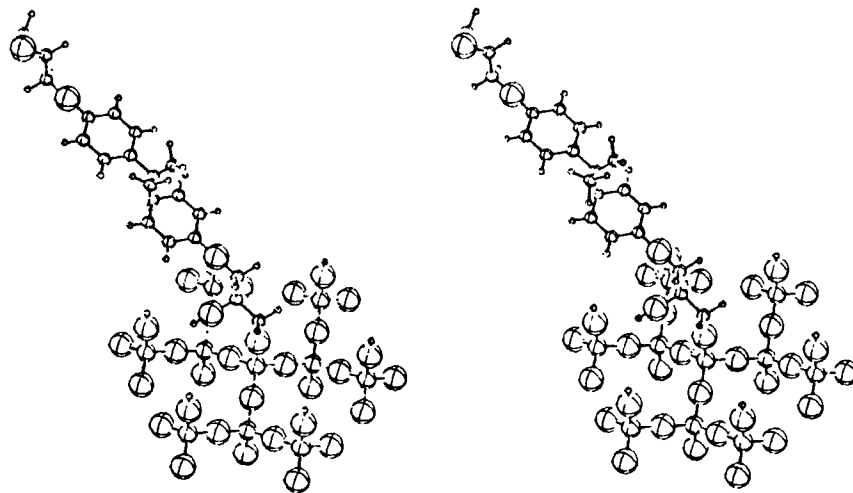


Figure 4. Stereo pair of epoxy molecule bonded at surface of hydrated silica.

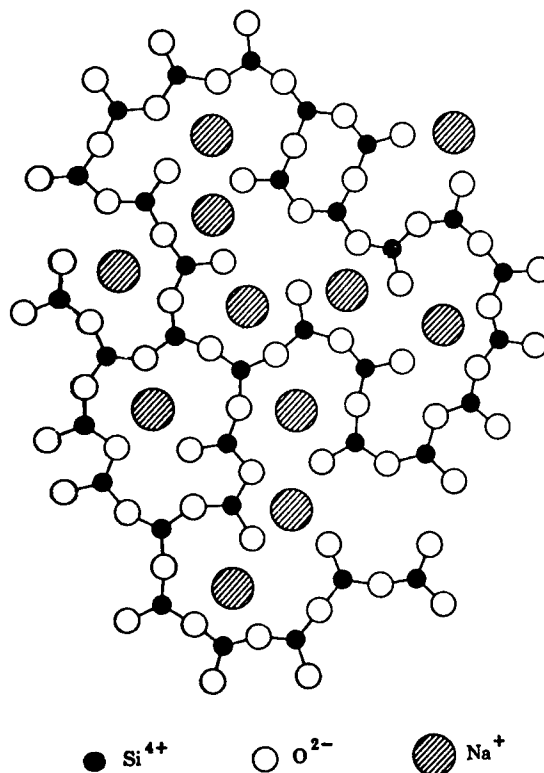


Figure 5. Schematic Representation of a sodium silicate glass, (B.E. Warren, J. Am. Cer. Soc., 24, (1941) 256).

diameters of the spheres and the rods connecting the spheres are chosen to enhance the illustration, and are not expected to completely portray phase orbital bonding in the system.

There are other variations of this illustration from the real materials. In the real composite, the polymer molecules extend much further, including many thousands of atoms interconnected in the phase. Furthermore, the conformation of the molecular branches at the surface of the glass varies considerably from that shown here with many different conformations existing. The density of attachment of the branches at the maximum is with a closest spacing of 5.62Å, allowing approximately 7.5 attachments per 100Å². However not all sites are occupied. In addition to the polymer molecules, there is a residual distribution of curing agent molecules that is non-uniformly distributed through the system.

The structural glasses are amorphous rather than crystalline as shown here, but the variations in structure are not pronounced over the short range of the volume element that is illustrated here. Figure 5 is a typical illustration that is used by many authors to represent the structure of a glass. The implication is that the continuity of the matrix is interrupted and the number of neighbors is altered in local regions due to substitution by cations of different valence for the silicon in the matrix, and various rotations about the silicon-oxygen or metal-oxygen, atomic bonds to accommodate the variation in sizes and connectivities that are involved. These changes in structure are reflected in changes of density, elastic properties, and chemical reactivities.

Cooper and Krohn (17, 18) are representative of several investigators who have looked into the possibility of strengthening glass fibers by modification of surface structure or addition of surface layers of other compositions.

D. Summary of Initial Status

In view of these various concepts and results, it was known that the glass was one of the more reactive components in the system, and it was realized that a number of variables were important or contributed to the overall properties and stability of the system. It was not known, however, whether the glass was the most reactive component or possibly the only reactive component in the system, and it was necessary to develop a line of experimentation to clarify the relative importance of the different contributing factors. Previous work by Jemian and Wilcox showed that mechanical properties of the glass, as well as those of the composites, were affected adversely by exposure to humidity, but that properties could be stabilized and possibly recovered by prolonged exposure. (19). The specific needs for the continuation of the research to identify the degradation process and its stages and nature were for a standard sample that had a major proportion of glass, analytical and various test methods that would afford a direct evaluation of the progress of the reaction, a means to control the environmental conditions, and more information and control on the nature of the finish material.

The intended direction of the research was to identify which of the factors above was most important in the degradation, and to set forth a plan to find methods to stabilize the composites to retain the desirable mechanical properties.

II. EXPERIMENTAL PROCEDURES

A number of separate experiments were conducted in connection with this research. In some the procedures are different and distinct from those of the others and in other cases the procedures are common to several. They will be described in a chronological order in this portion of the report. The results will be summarized and interpreted in the next portion of the report, III RESULTS AND DISCUSSION.

The basic approach to the degradation study was to examine the nature and properties of the individual materials constituents of the system and then finally to examine the properties of the composite. Initial work, begun in connection with an earlier project, involved considerable investigation into the mechanical strengths of the individual glass filaments. This pursuit was set aside temporarily but resumed in the latter half of the contract period. It was realized that the properties of the composite are strongly related to the filament properties. Test procedures and new results are explained in this section and are followed by descriptions of experiments of heat treatment and surface preparations on the properties of the individual glass filaments.

The last experiments described are concerned with the composite samples in the strand tensile configuration and related studies.

A. Single Filament Test

In processing data for the single filament test the assumption

was made that "within the range of variation of diameter in these samples the structure of the glass and its bulk properties are independent of this sample diameter. Bulk properties, such as elastic modulus and specific gravity depend upon the atomic species which is constant and the molecular structure which is homogeneous. Therefore, in processing the data it was assumed that any variation of the slope of the curve could be attributed directly to the variation in sample diameter." And further "this procedure calls for an additional assumption, namely that the fracture mechanism is not affected by filament diameter. Again, over this range of filament diameter the number and types of crack nuclei will not differ." (19, page 31) It was decided to experimentally verify these assumptions.

The Single Filament Test provides a direct means to measure the mechanical properties of a glass fiber sample in tension. Each sample, which may have a diameter approximately $1/5$ that of a human hair is attached to a grip using an organic solder (diphenylcarbazine). The grips are conveniently made by bonding U shaped loops of resistance wire in 4-hole thermocouple protection tubes with an epoxy adhesive. Two configurations are illustrated in Figures 6 and 7. In the first, simpler type of grip the solder is melted around the curve of the loop by passing an electrical current through the wire. When the solder is liquid, the sample is touched to the droplet and is pulled in and held by surface tension forces. It is frozen in when the current is stopped. In the second design the solder is melted along the two vertical parallel

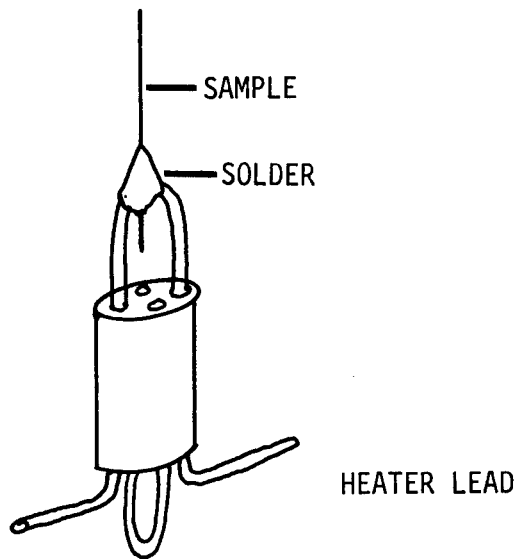


Figure 6. Single filament mechanical testing grip, simple loop style.

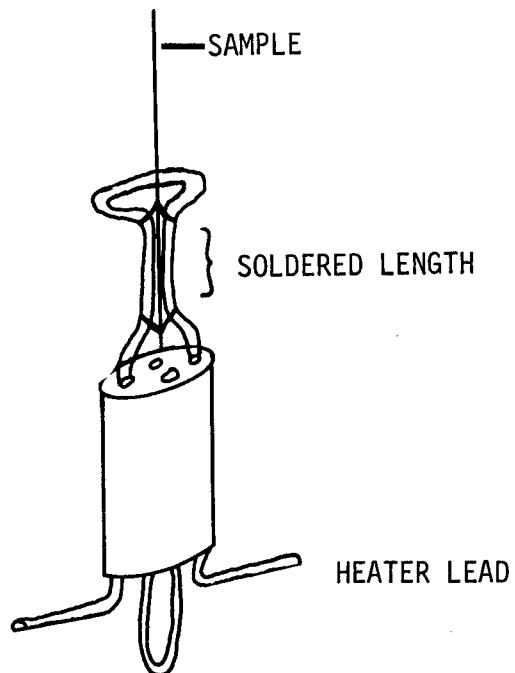


Figure 7. Single filament grip, parallel support type.

branches of the loop and the sample is again held in the liquid by surface tension. With this grip design the sample is held more nearly along a center line of the loading system and over a longer length of contact. This second design is planned to reduce the machine deformation component which is primarily in the grips at the low maximum testing loads encountered.

The test procedure involves sample selection, mounting and measurements and finally testing. Each will be described separately below:

Sample selection involves removing an individual filament from the roving and measuring its diameter using a filar micrometer eyepiece in a metallurgical microscope at 250 diameters magnification. Diameters are measured at 3 points along the sample. Cross hair positions are recorded on both sides of the sample at each of the three locations. If the diameters at these locations vary more than 3%. The determination is repeated or the sample is discarded.

The sample is attached to the upper grip first as a matter of convenience and then to the lower grip. Each sample is tested twice with two different gage lengths. The gage length is determined by the extension scale on the testing machine. The results are subtracted so that the increment in gage length between the two tests represents the sample and is independent of machine deformation component.

The test is performed by loading the sample to approximately three quarters of full scale unless the sample breaks prematurely.

The sample can then be unloaded and reattached with a shorter gage length and the test repeated. It is not necessary to run the sample to the breaking point unless the breaking strength information is required. After the test the sample is detached from the grips and saved on a piece of colored computer paper with two sided scotch tape.

A series of samples were processed following an earlier, abbreviated procedure. The results confirm the absence of a systematic effect of sample diameter. The measured average modulus and tensile strengths over a range of 353 to 508 μ in. are 182 ksi and 9.25 msi, respectively. Tests, using the two-gage procedure were adopted in order to be able to obtain an absolute, rather than only relative measure of elastic modulus. The modulus determined by the 2 gage length method is 13.02 msi. Figure 8 shows a typical load-elongation curve for a glass filament.

B. Heat Treatment

For a complete investigation of the water degradation of glass fibers, the original coupling agent must be removed to eliminate possible errors in analysis and to examine the effects of other coatings on degradation rate. Burning off of the coupling agent at 550°C for one-half hour is one possible method of removal. Therefore, an investigation was conducted to determine if the necessary heat treatment required for removal of the coupling agent causes devitrification or other detrimental structural changes in the glass. S-glass in both fiber and bulk form and bulk E-glass were used in

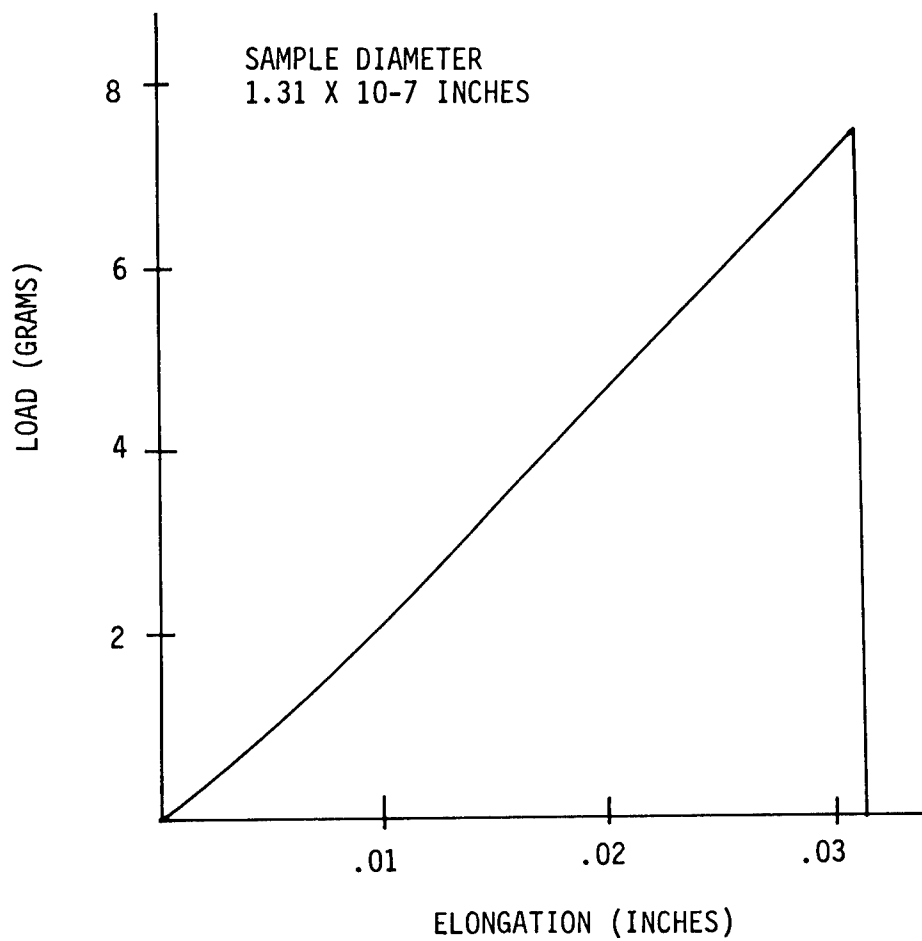


Figure 8. Typical load-elongation chart record of single filament test.

this investigation. The glass was furnished in the form of a multi-filament roving. The bulk glass was in marble form. Examination of the glass involved both optical and replica transmission electron microscopy techniques.

Preliminary work with S-glass fibers showed that fibers were not suitable for this investigation. To examine the structure of glass fibers in cross section, the fibers had to be mounted. Cold mounting techniques were used to eliminate possible effects of pressure and heat involved in hot mounting processes. This investigation also involved the effects of boiling water on the structure of the heat treated glass. Boiling was performed after the fibers were mounted in order to monitor the same structure throughout various treatments. Therefore, the mounting material had to meet several requirements: 1. cure at room temperature, 2. have good bonding with the glass, 3. be inert to acetone used in the replication process, 4. be hard enough not to smear over the fiber surface during polishing, 5. be inert during boiling, and 6. be inert to HF used to etch the glass. Various epoxies were used for cold mounting and in all cases one or more of the above requirements could not be met.

Figures 9, 10, and 11 illustrate the effect of cutting the mount to obtain a flat surface and subsequent etching of the glass with 5% HF. Cutting of the mount smears epoxy over the glass surface which interferes with the replicating process and produces artifacts. Etching with 5% HF for times up to 10 minutes seems to have little or no effect on the structure. Mechanical polishing and etching



Figure 9. Electron micrograph of S-glass fibers cold mounted in epoxy and cut. 5586X



Figure 10. Electron micrograph of S-glass fibers cold mounted in epoxy, cut and etched 1 minute in 5% HF. 1482X

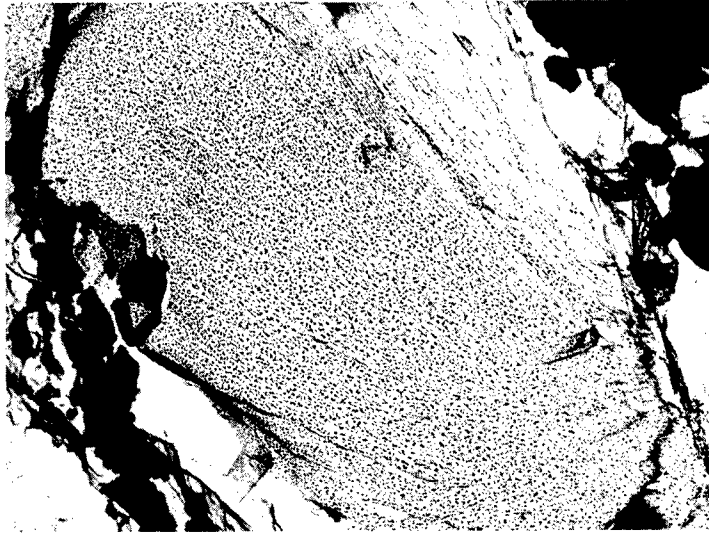


Figure 11. Electron micrograph of S-glass fiber cold mounted in epoxy, cut and etched 10 minutes in 5% HF. 12,540X

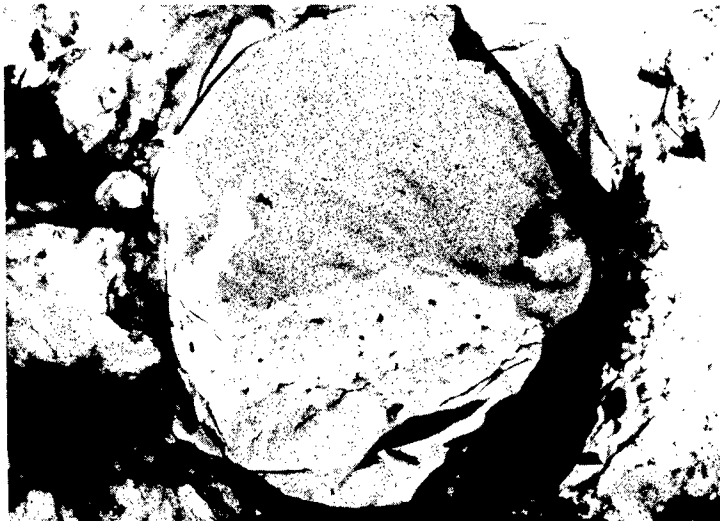


Figure 12. Electron micrograph of S-glass fibers cold mounted in epoxy and polished. 8094X

of the mounted fiber did not improve results, as is shown in Figures 12 and 13. The smeared epoxy on the fiber surface produced during polishing could not be removed completely by etching. The only noticeable effect observed on the fibers was the result of boiling the mounted fibers in water for three days after etching in 5% HF for one minute. Figures 14 and 15 show that boiling in water seems to smooth off the fiber surface indicating reaction of the glass with water. However, it could not be determined whether this effect was reaction with the water or just the removal of the smeared epoxy from the cutting operation.

In an effort to eliminate the problems involved with mounting of the fibers, bulk E-and S-glasses were then used in the heat treating investigation. Figures 16, 17 and 18 show the effect of heat treating S-glass at 800°C for four and 96 hours. No change in structure is evident as a result of either time of heat treatment or cooling rate after heat treatment. The same results were obtained with bulk E-glass for the same annealing times at 800°C, see Figures 19, 20 and 21. From these micrographs, it is evident that annealing up to 800°C has not caused devitrification of either S-glass or E-glass.

In addition to the heat treating experiments, bulk glass was boiled for seven days in distilled water before and after annealing at 800°C for four hours. Figures 22 to 25 show the effects of boiling on S-glass and E-glass, respectively. The structure of the as-received glass boiled for seven days in both cases does not differ from the annealed structures. Annealing for four hours at

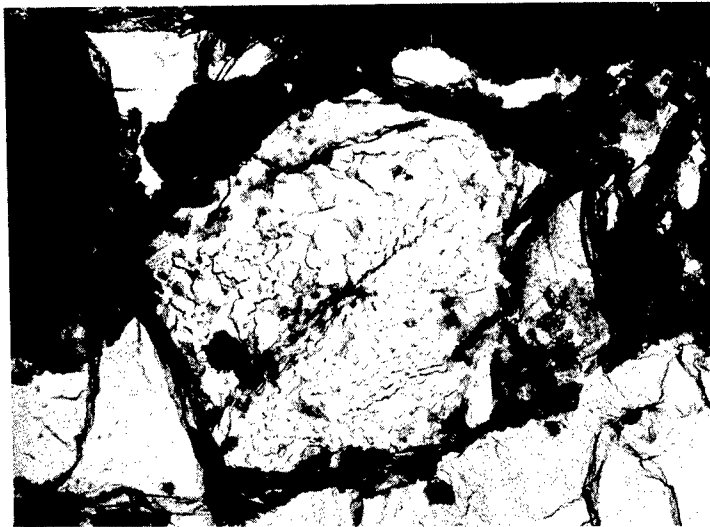


Figure 13. Electron micrograph of S-glass fiber cold mounted in epoxy, polished and etched 1 minute in 5% HF. 10,260X

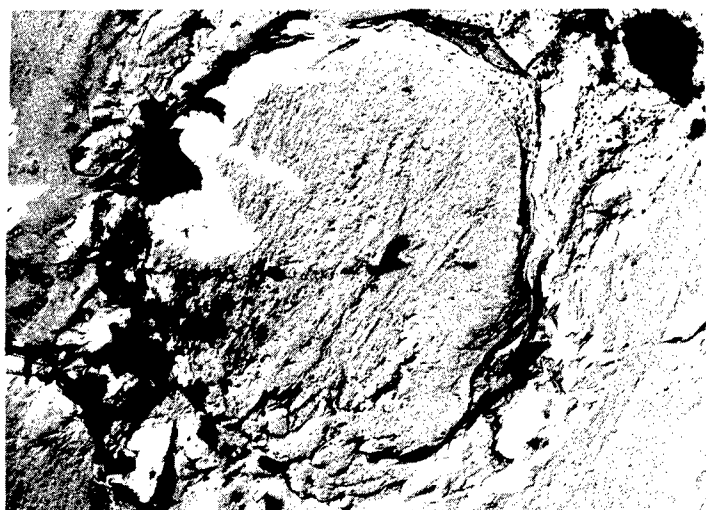


Figure 14. Electron micrograph of S-glass fibers cold mounted in epoxy, cut and boiled 3 days in distilled water. 5586X

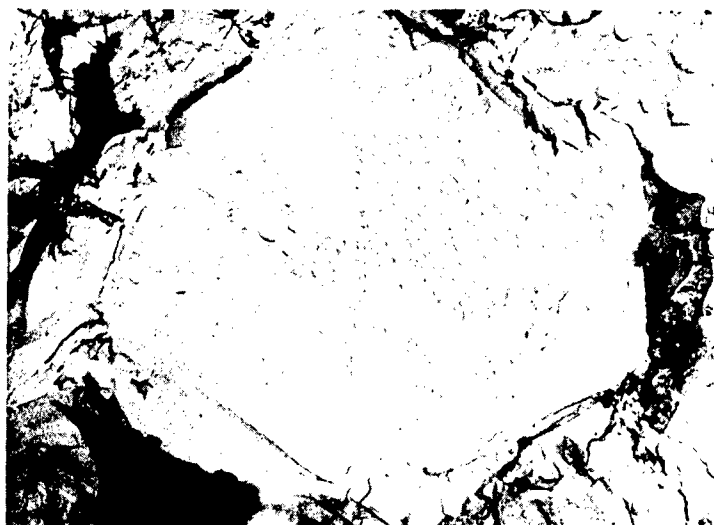


Figure 15. Electron micrograph of S-glass fibers cold mounted in epoxy, cut, etched 1 minute in 5% HF and then boiled 3 days in distilled water. 8094X

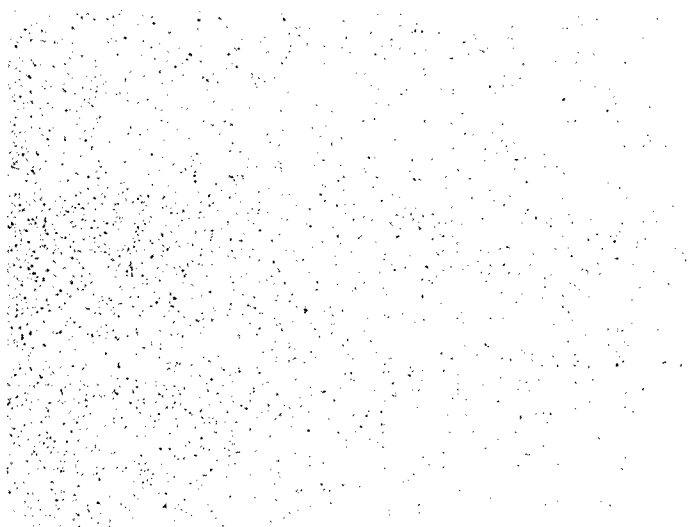


Figure 16. Electron micrograph of bulk S-glass heat treated 4 hours at 800°C, furnace cooled, polished and etched 5 minutes in 5% HF. 39,900X

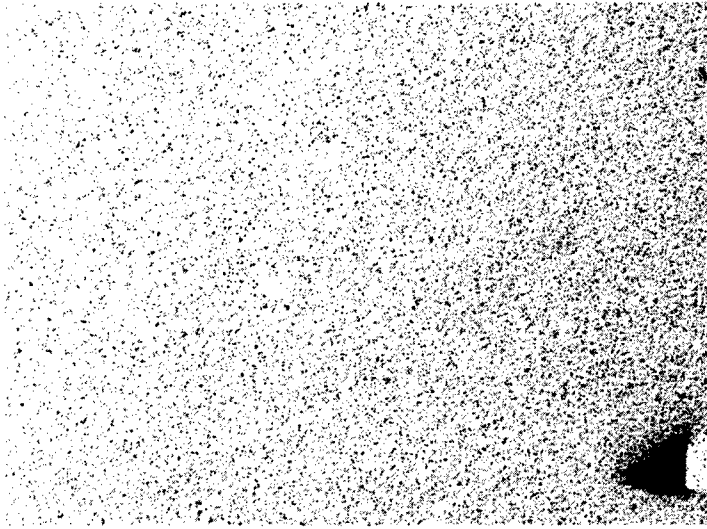


Figure 17. Electron micrograph of bulk S-glass heat treated 96 hours at 800°C, air cooled, polished and etched 1 minute in 5% HF. 39,900X

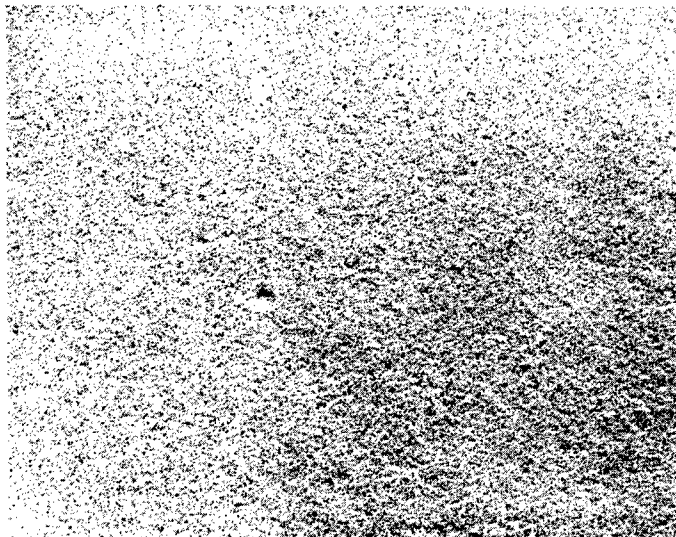


Figure 18. Electron micrograph of bulk S-glass heat treated 96 hours at 800°C, air cooled, polished and etched 10 min. in 1% HF. 39,900X

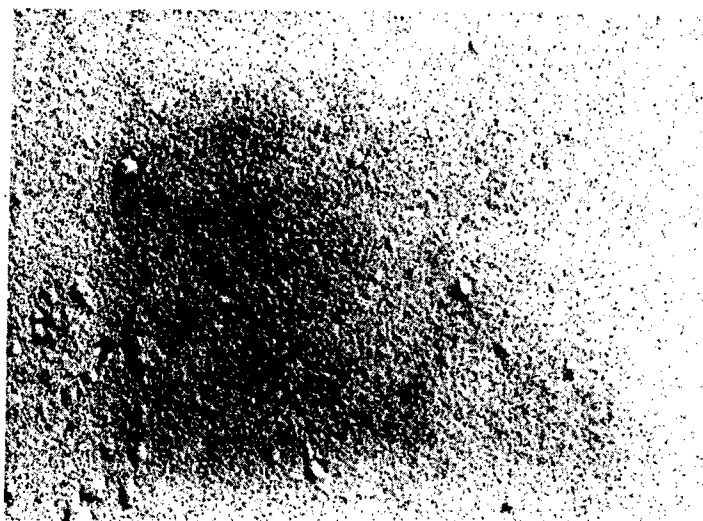


Figure 19. Electron micrograph of as-received bulk E-glass, polished and etched 1 minute in 5% HF. 39,900X

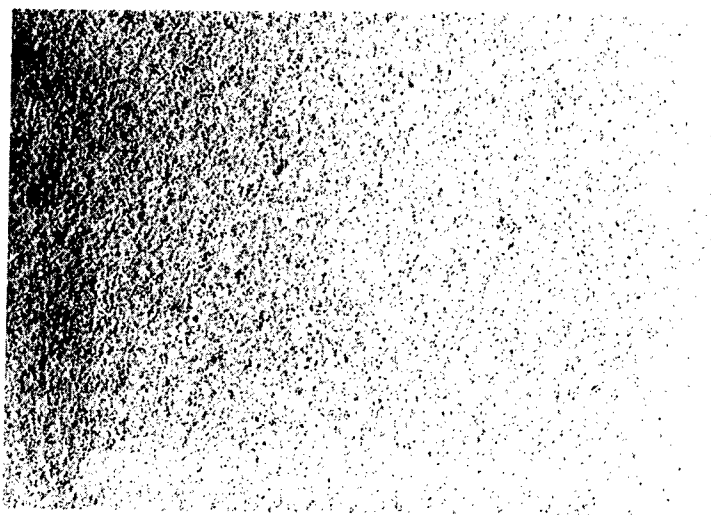


Figure 20. Electron micrograph of bulk E-glass heat treated 4 hours at 800°C, furnace cooled, polished and etched 5 minutes in 5% HF. 39,900X

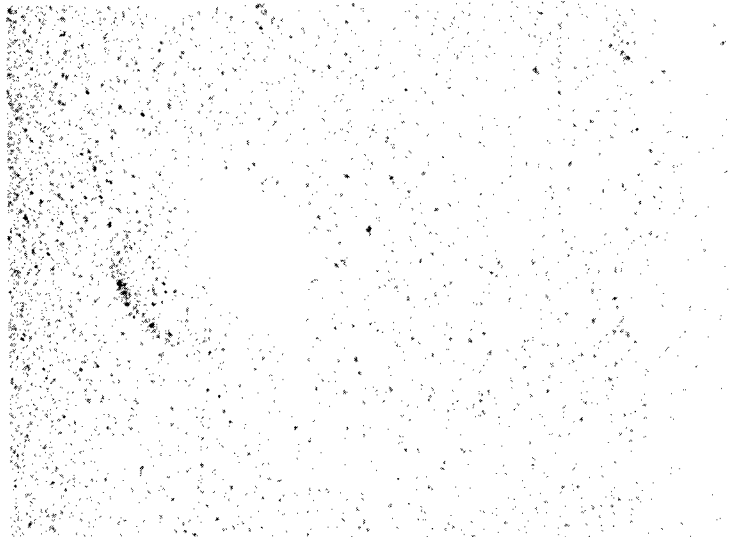


Figure 21. Electron micrograph of bulk E-glass heat treated 96 hours at 800°C, air cooled, polished and etched 1 minute in 5% HF. 102,600X

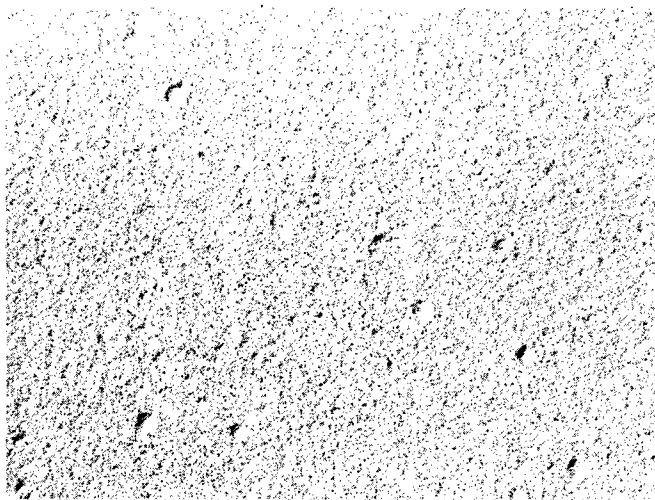


Figure 22. Electron micrograph of as-received bulk S-glass boiled 7 days in distilled water. No etchant. 39,900X

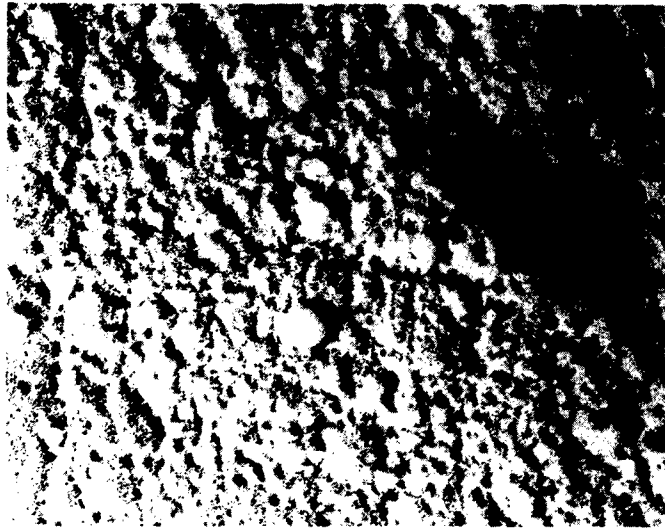


Figure 23. Electron micrograph of bulk S-glass heat treated 4 hours at 800°C and boiled 7 days in distilled water. No etchant. 39,900X

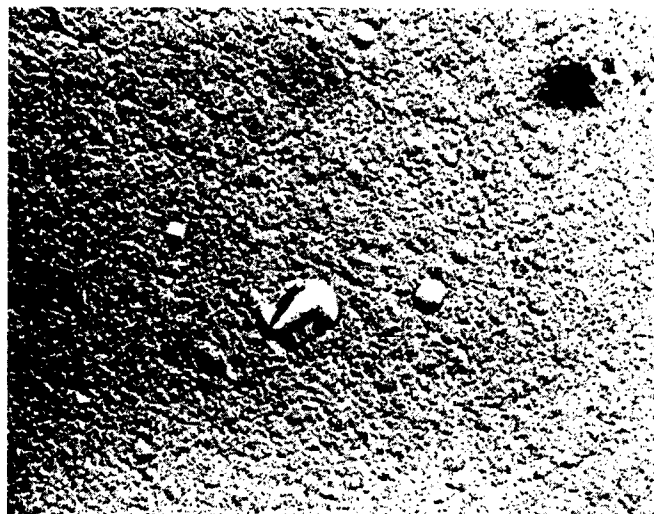


Figure 24. Electron micrograph of as-received bulk E-glass boiled 7 days in distilled water. No etchant. 39,900X

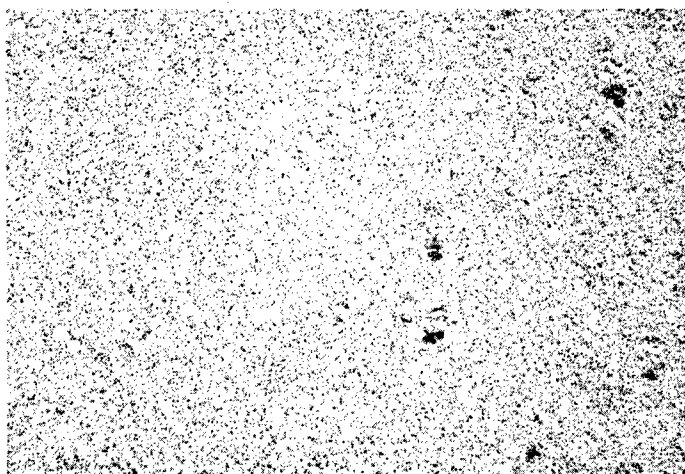


Figure 25. Electron micrograph of bulk E-glass heat treated 4 hours at 800°C and boiled 7 days in distilled water. No etchant. 39,900X



Figure 26. Scanning electron micrograph of as-received S-glass fibers (Ferro). 1200X

800°C prior to boiling in water for seven days seems to have little effect. The surface of the S-glass, see Figure 23, is somewhat rougher. The surface of the E-glass, see Figure 25, does not seem to have changed. These results indicate that annealing of the glass at 800°C may have some small effect on the reaction rate with water.

The evidence of no microstructural change as a result of heat treating at 800°C is in agreement with Gregory and Veasey (10-13). They found by differential thermal analysis that crystallization in cordierite ($\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ with approximately 50% SiO_2) does not occur below about 980°C even with nucleating agents such as TiO_2 . Since annealing at 800°C does not cause any visible microstructural changes, a heat treatment of one-half hour at 550°C to remove the coupling agent should not be detrimental to the glass structure or properties.

C. Surface Preparation

In preparation for the investigation of the effects of various coupling agents on the rate of water degradation of glass in fiber-glass composites, some means of stripping the coating present on the as-received fibers is necessary. This surface preparation of the glass fibers must not only remove the original coating, but also must not be detrimental to either the structure or properties of the fibers. Consequently, an investigation was conducted to determine the best method of surface preparation of the glass fibers.

S-glass fibers furnished by both Owens-Corning and Ferro Corporation were utilized and the results analyzed using scanning electron

microscopy, differential thermal analysis, and thermogravimetric analysis techniques. Four surface treatments were given considerable attention. These treatments were 1. As-received, 2. heat treated 0.5 hours at 550°C, 3. washed in acetone, and 4. washed in aqua regia.

1. Microscopy

S-glass fibers in the various treated conditions were mounted on aluminum holders and coated with an Au-Pd alloy to reduce discharging in the electron beam. Figures 26-29 compare the results obtained with S-glass fibers from one batch. The coating on the as-received fibers is quite thin and cannot be resolved. Little if any difference is seen in the fibers after annealing at 550°C for 0.5 hours or washing for 22.5 hours in either acetone or aqua regia. No apparent effect on the surface of the fibers is visible as a result of these surface treatments.

Figures 30-33 show the results of the same four treatments on S-glass fibers from a separate starting glass. Again the coating on the as-received fibers is thin and cannot be resolved. After annealing for 0.5 hours at 550°C, the fibers apparently remain clean. However, when washed for 23.5 hours in either acetone or aqua regia, some residual coating is visible. This seems to indicate that the original coating is uniformly thin over the fibers. Washing in acetone or aqua regia only partially removes this original coating, and that part which remains can be resolved. These results were not obtained with the fibers from one source which indicate that the original coating on the other fibers is thicker



Figure 27. Scanning electron micrograph of S-glass fibers (Ferro) annealed 0.5 hours at 550°C. 1680X

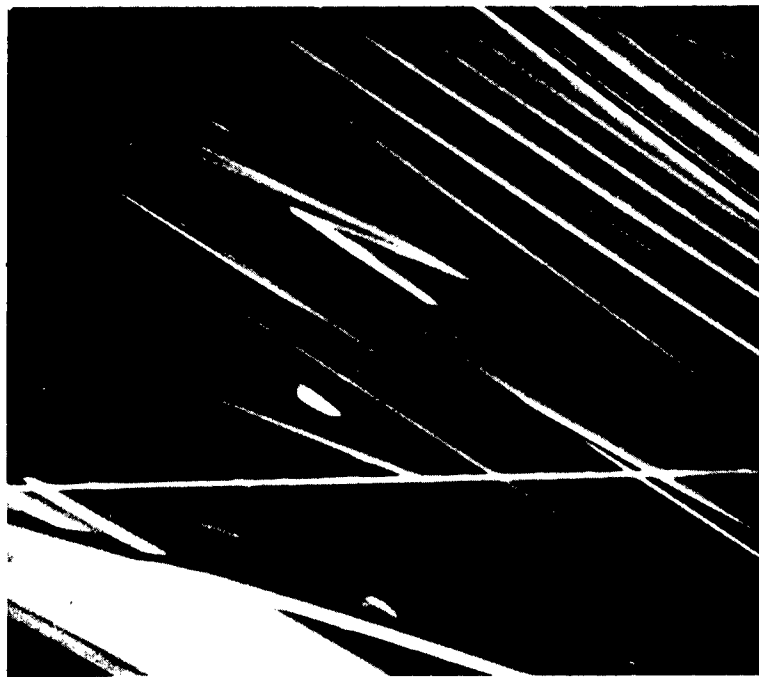


Figure 28. Scanning electron micrograph of S-glass fibers (Ferro) treated 22.5 hours in acetone. 325X

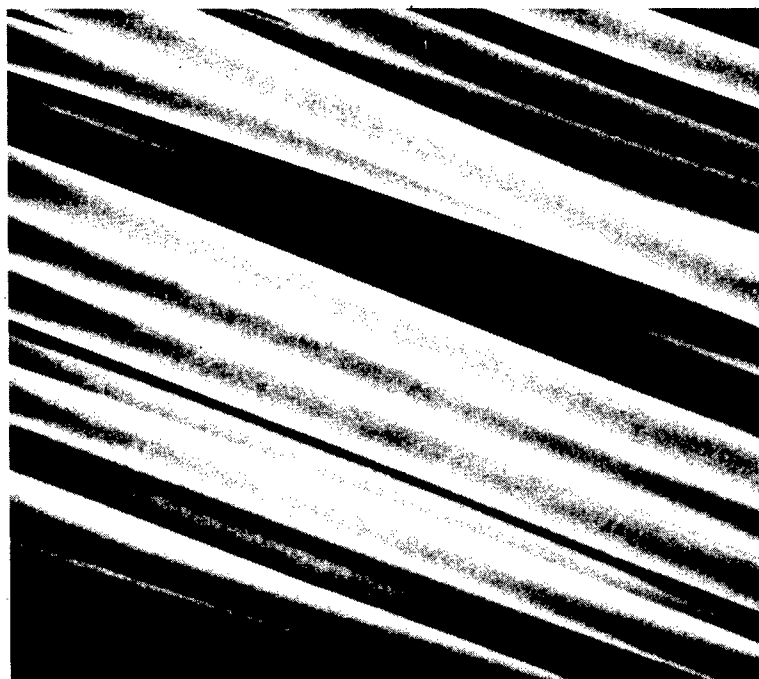


Figure 29. Scanning electron micrograph of S-glass fibers (Ferro) treated 22.5 hours in aqua regia. 580X



Figure 30. Scanning electron micrograph of as-received S-glass fibers (Owens-Corning). 1760X

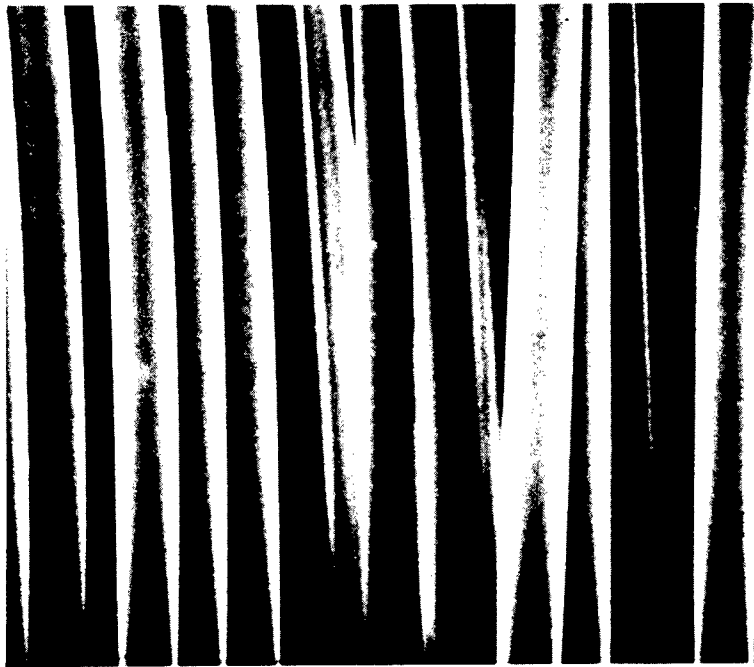


Figure 31. Scanning electron micrograph of S-glass fibers (Owens-Corning), annealed 0.5 hours at 550°C. 900X



Figure 32. Scanning electron micrograph of S-glass fibers (Owens-Corning) treated 23.5 hours in acetone. 1000X

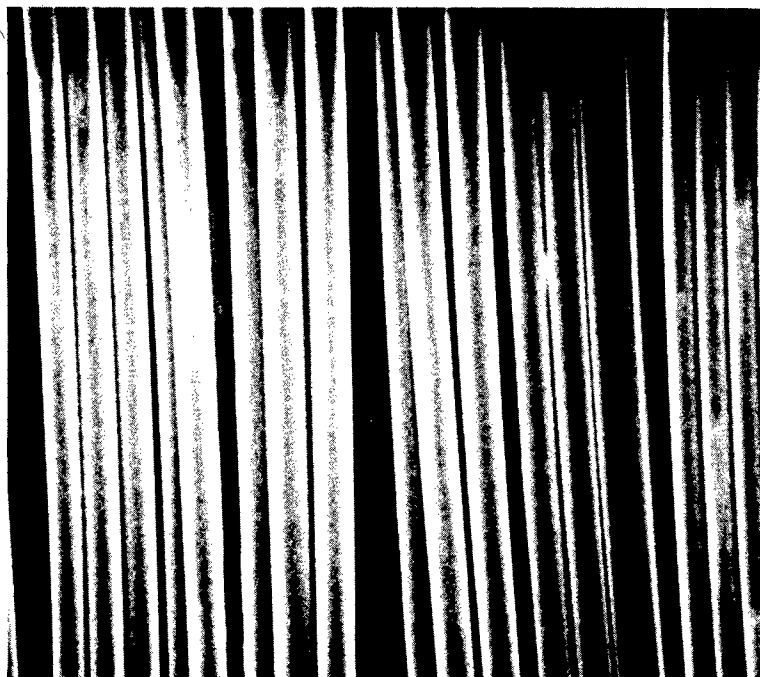


Figure 33. Scanning electron micrograph of S-glass fibers (Owens-Corning) treated 23.5 hours in aqua regia. 490X

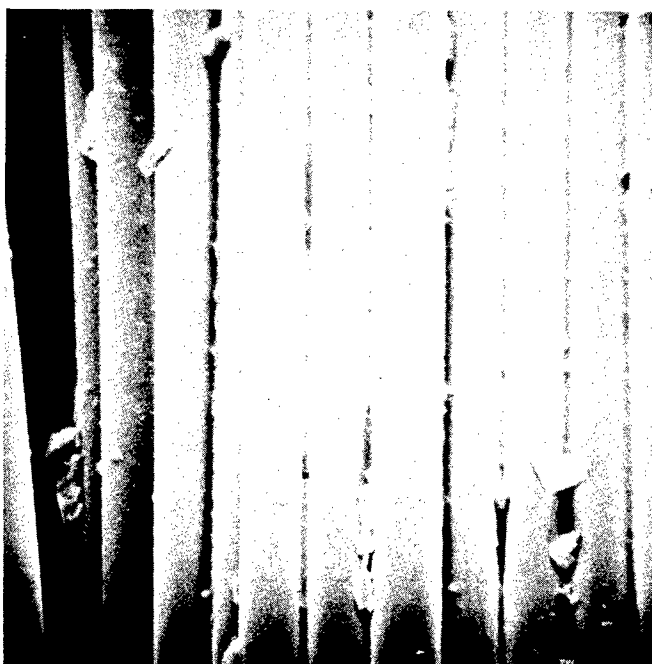


Figure 34. Scanning electron micrograph of Owens-Corning as-received S-glass fibers used in previous contract. 1060X

and the chemical treatments more effective.

At this point, a comparison must be made between the S-glass fibers used for this investigation and the fibers of the same batch originally used in a previous contract (7). Figure 34 shows as-received fibers used for the previous contract. A considerable difference is seen between the as-received fibers in Figure 30 and Figure 34. These fibers were taken from different rovings of S-glass and indicate that product has probably changed processes during this interval.

2. Differential Thermal Analysis

Because of the inconclusive results of the microscopic examination, differential thermal analysis (DTA) was used in an effort to evaluate more effectively the results of the various surface treatments. In this analysis, the change in temperature within a sample resulting from either endothermic or exothermic reactions is measured against a standard. The greater the change in temperature, the greater the reaction which occurs. All samples were analyzed continuously with a programmed rate of 20°C per minutes from room temperature to 600°C in air. Since structural changes within S-glass occur at higher temperatures (10-13) the only reaction which should then occur below 600°C involves the burning off of the coating. Comparison of the extent of the temperature change with surface treatments gives an indication of the effectiveness of these treatments. A Dupont Differential Scanning Calorimeter was utilized in this investigation.

Two completely different thermal analyses were performed. The first analysis involved cutting the fibers to fit the 0.25 inch diameter sample holder and using an empty holder for the standard. Only two to five milligrams of glass could be analyzed per sample by this procedure because the fibers could not be packed efficiently in the sample holder. The second method utilized ground glass fibers and calcined alumina as the standard. Approximately 8.5 to 9.5 mg was used in the latter method. Aluminum sample holders were used in all runs. In all cases, the observed peaks below 100°C result from thermal stabilization of the system.

The results of the DTA investigation using short lengths of glass fibers (approximately 1/16 inch) and an empty pan standard are shown in Figures 35-37. As a result of using fibers and not ground fibers, the mass per sample varied from 2.4 to 5.1 mg. This large variation in mass required that the data be normalized to eliminate the effect of mass. Normalizing was performed every 50°C from 250° to 600°C. The resulting curves were then produced as straight lines between points to give the general shape of the curves.

From Figure 35, S-glass in the as-received condition shows a strong reaction between 300 and 600°C which results from the burning off of the coating. Annealing at 550°C for 0.5 hours, or washing the fibers in acetone or aqua regia for 22.5 hours seems to have removed most of the coating. The aqua regia wash in this case seems to be the most effective.

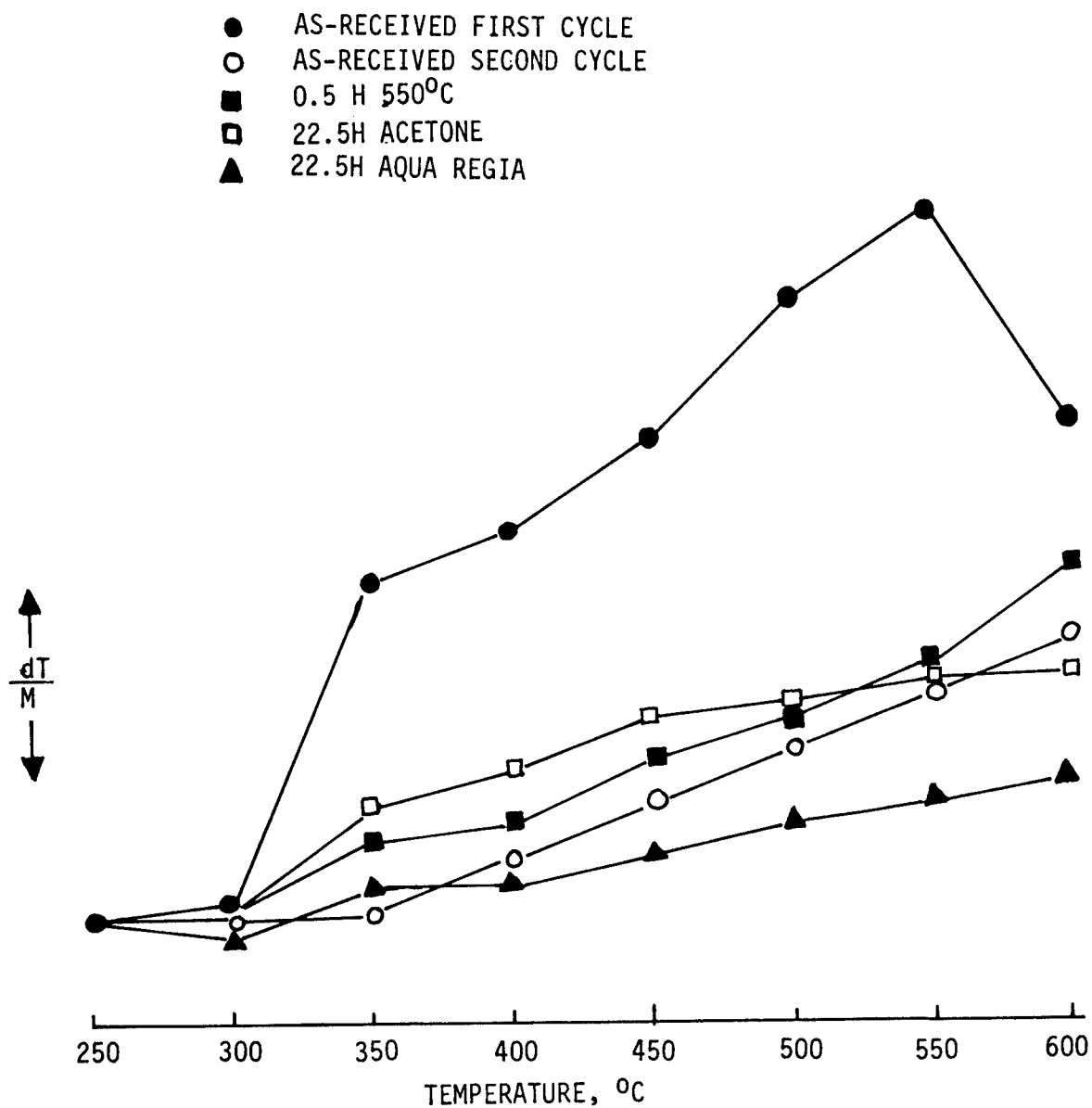


Figure 35. DTA curves for Ferro S-glass using short fibers and an empty pan standard.

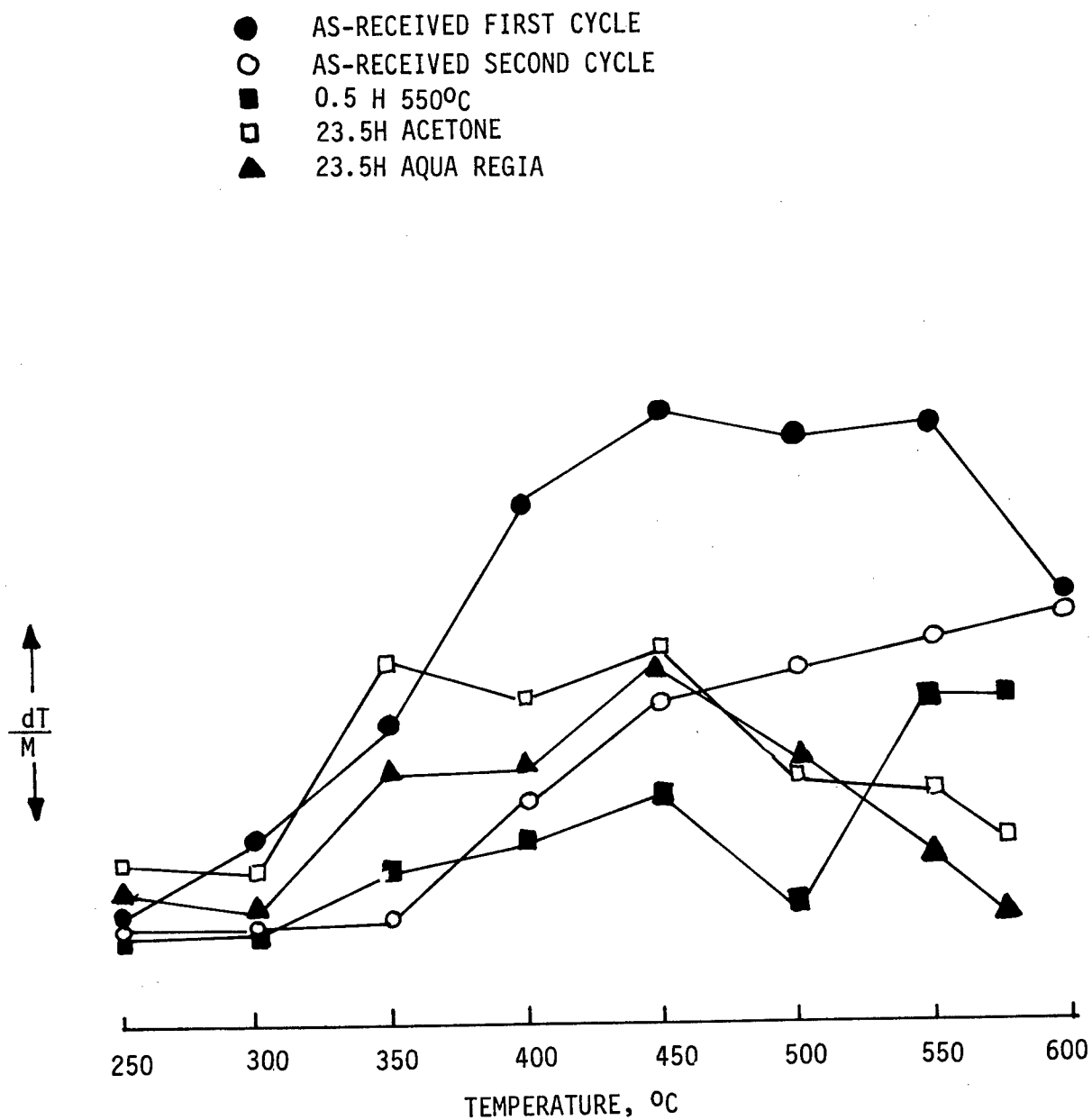


Figure 36. DTA curves for Owens-Corning S-glass using short fibers and an empty pan standard.

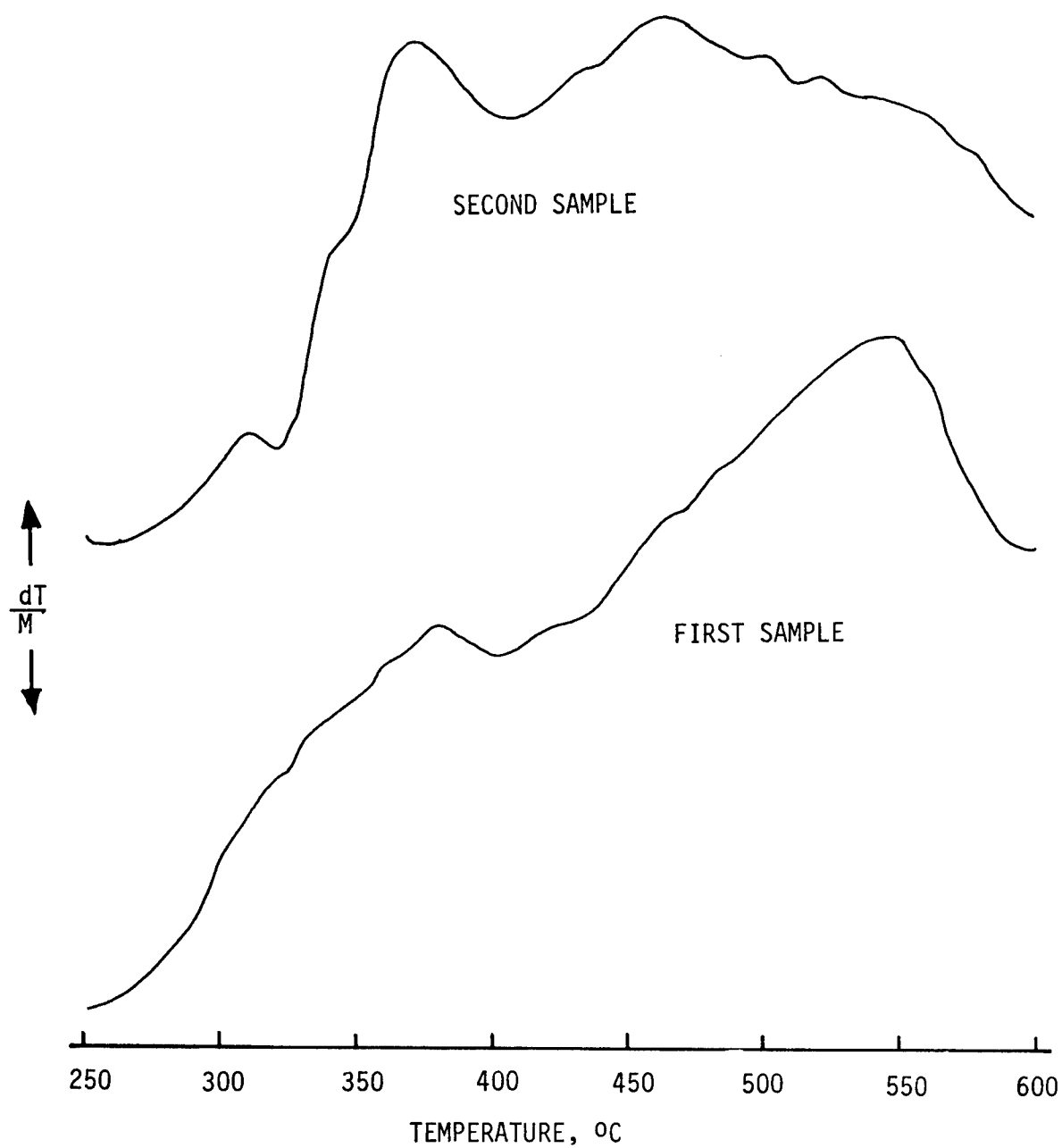


Figure 37. Comparison of DTA curves for as-received S-glass using short fibers and an empty pan standard.

Greater scatter was obtained with the other batch of S-glass, Figure 36. Again the greatest reaction occurred with the as-received fibers, with the various treatments reducing the reaction. In this case, the most effective treatment seems to be annealing at 550°C for 0.5 hours.

Figure 37 shows the DTA data for both the groups of as-received S-glass. In this case the data is normalized every 10°C instead of 50°C for better comparison of the two glasses. In both cases, the exothermic reaction is divided into two peaks, the first and sharpest peak occurring between 340 and 360°C. The broadest peak occurs between 400 and 600°C. This second peak is broader in the second glass sample. The comparison of these two curves indicated that the coupling agent (coating) is somewhat similar in both cases, but probably varies in composition.

After analyzing the DTA curves obtained from short fibers and an empty pan standard, it was felt that more and better information was necessary to draw any logical conclusion concerning the various surface treatments. Therefore, the standard was changed to calcined alumina which is considered to be one of the best and was utilized by Gregory and Veasey (12) in their work with Cordierite glass. In an effort to increase the sample size and thus have a better chance of observing any reaction which might occur, the glass fibers were ground. This allowed better packing of the sample in the holder. Figures 38 and 39 show the approximate length of glass fibers which could be obtained by grinding. The ground glass fibers in Figure 38 were obtained by minimum grinding to break

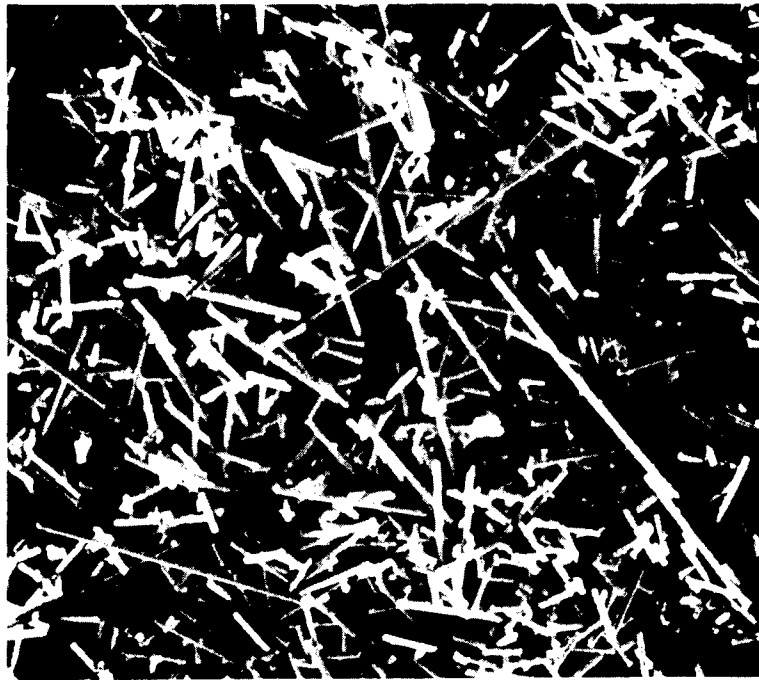


Figure 38. Scanning electron micrograph of S-glass fibers annealed 0.5 hours at 550°C and then ground. 82X

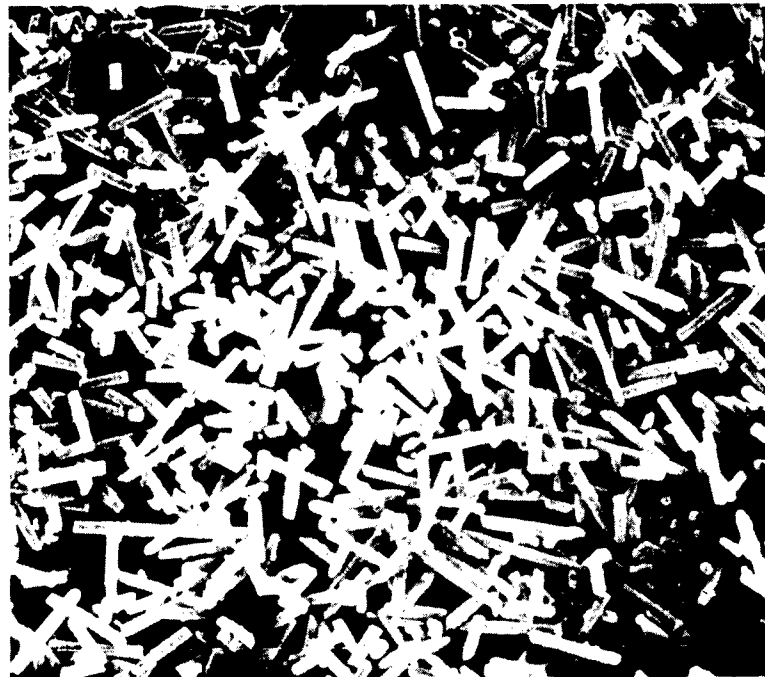


Figure 39. Scanning electron micrograph of S-glass fibers annealed 0.5 hours at 550°C and ground to -300 mesh. 120X

up 1/8-inch long lengths. The glass in Figure 39 results from grinding to pass the fibers through a 300 mesh screen. Differential thermal analysis was then utilized to evaluate the effect of ground fiber length, see Figure 40. As a result of the extremely long preparation time (grinding) and the small difference in the DTA results, grinding to -300 mesh was not considered necessary. Thus, the following DTA results are based on minimum grinding of the S-glass fibers.

The results of the DTA investigation using ground S-glass fibers and calcined alumina standard are shown in Figures 41-43. With the use of the ground fibers, the mass per sample varied from 8.47 to 9.7 mg. This small variation in mass did not require normalizing the DTA data with respect to mass. The data, however, was normalized with respect to the baseline obtained with a calcined alumina sample. Normalizing was performed every 10°C and a smooth curve drawn between the normalized points. This resulted in far better shape and analyses of the curves.

From Figure 41, S-glass from the second batch in the as-received condition shows two strong reactions from burning off of the coating which peak at 420° and 480°C. Annealing at 550°C for 0.5 hours removes the coating entirely. Washing in either acetone or aqua regia for 23.5 hours is not very effective and compares favorably with the microscopy results. Aqua regia does seem to remove more of the original coating than acetone. These results are in general the same as shown in Figure 36 using an empty pan standard.

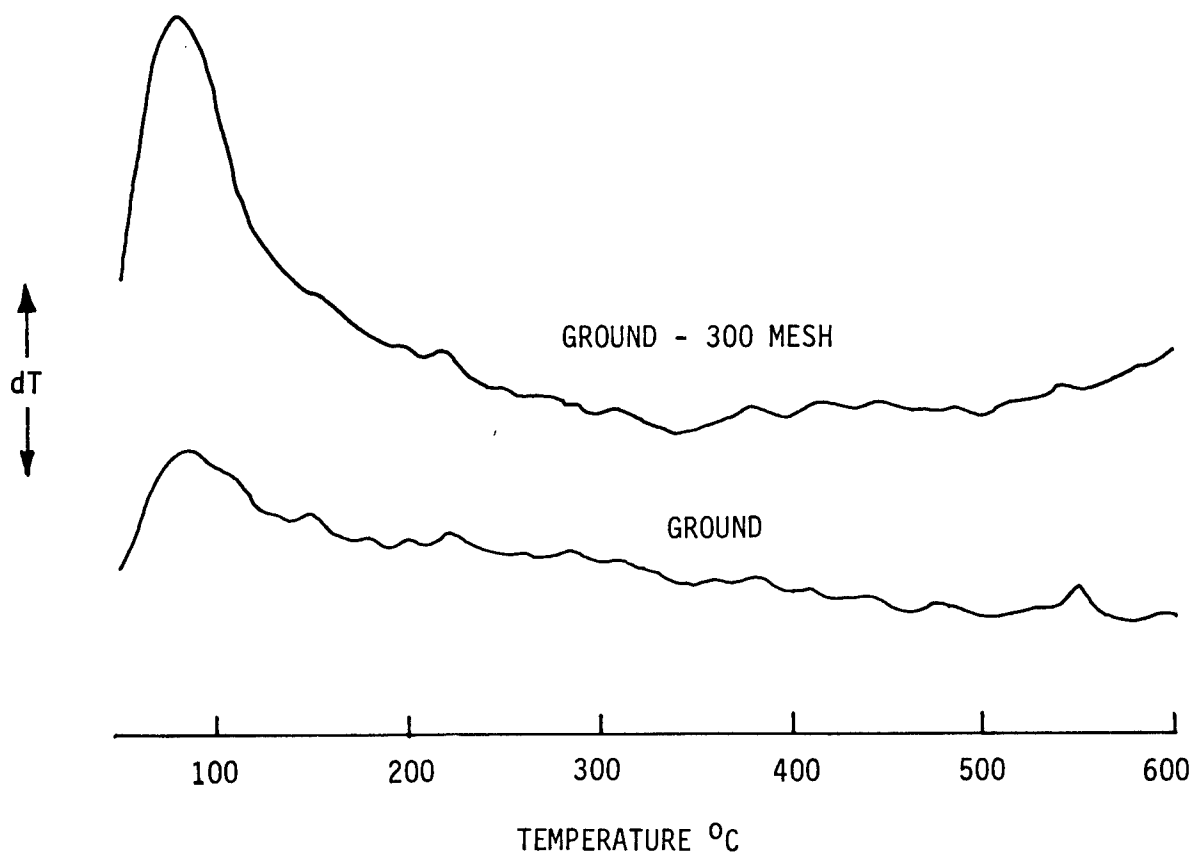


Figure 40. Comparison of DTA curves for ground Ferro S-glass fibers annealed 0.5 hours at 550°C using calcined alumina standard.

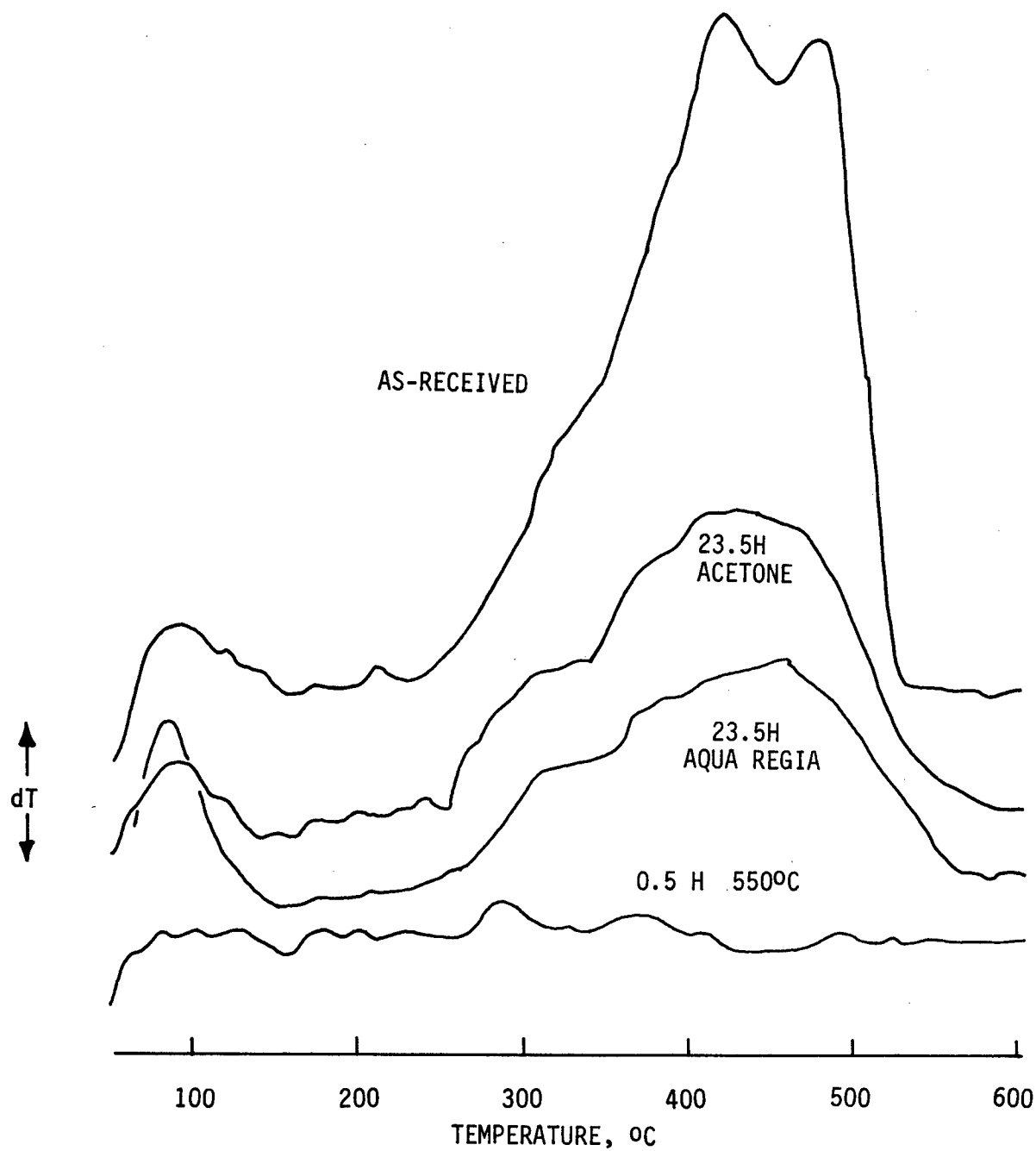


Figure 41. DTA curves for Owens-Corning S-glass using ground fibers and calcined alumina standard.

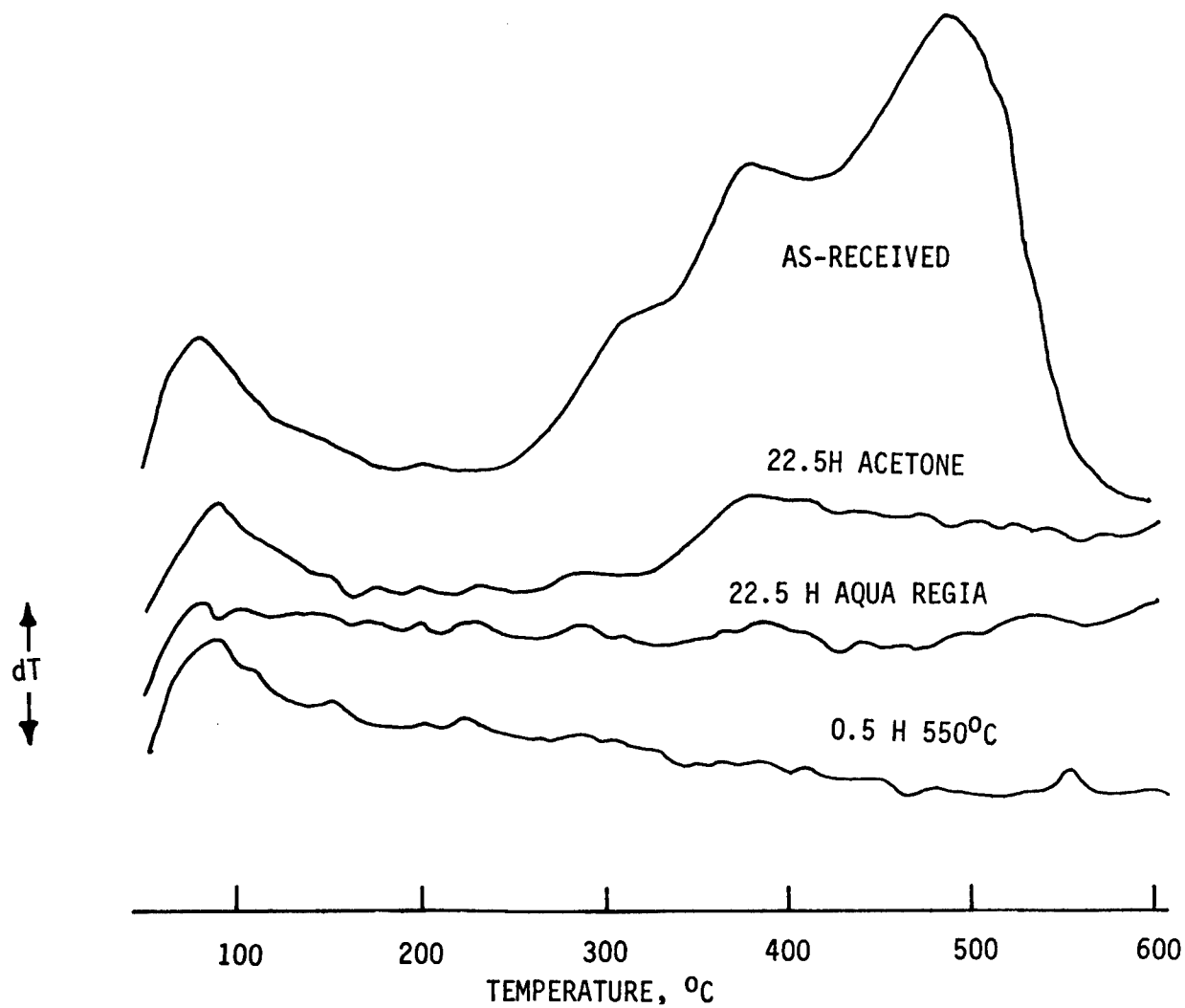


Figure 42. DTA curves for Ferro S-glass using ground fibers and calcined alumina standard.

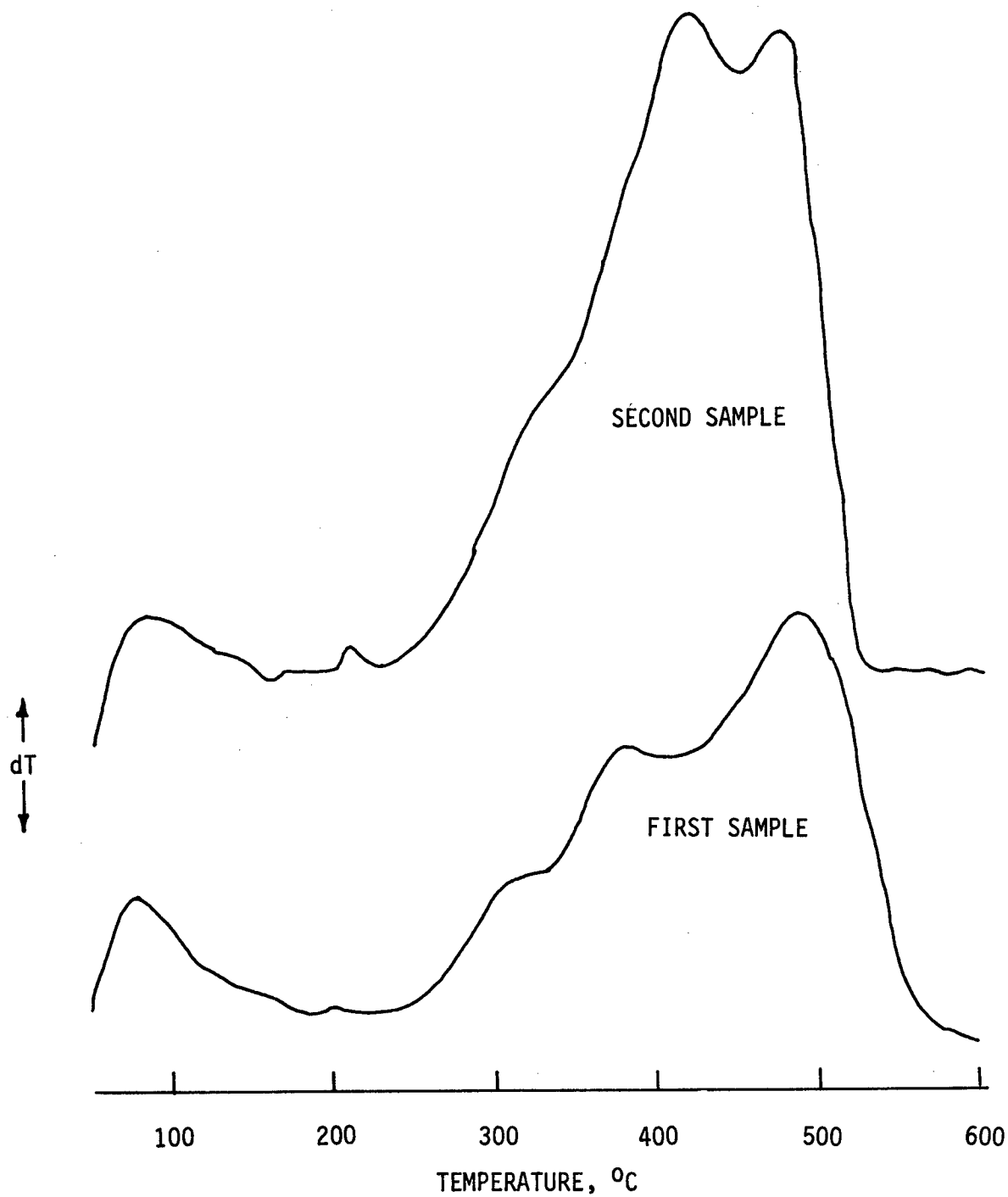


Figure 43. Comparison of DTA curves for as-received S-glass using ground fibers and calcined alumina standard.

However, the scatter in the data in Figure 41 is not as great as in Figure 36 and the results are more definite.

Figure 42 shows the DTA data for S-glass of the first batch. The burning of the coating of the as-received glass occurs over a wide temperature range and seems to consist of three peaks, 320, 380 and 490°C. Again, annealing at 550°C for 0.5 hours effectively removes the coating. Washing in either acetone or aqua regia for 22.5 hours is more effective in removing this coating than with the S-glass from the second sample. Even though aqua regia is better than acetone in this case, neither performs as well as annealing. These results are somewhat different from those in Figure 35 when an empty pan standard was used. Less scatter is observed in Figure 42 with more definite results obtained.

A comparison of the DTA data for both samples of S-glass in the as-received and ground condition is shown in Figure 43. As outlined above, the burning off of the coating results in two peaks, 420°C and 480°C, for the second sample S-glass and three peaks, 320°C, 380°C, and 490°C, for the first S-glass. Even though, in both glasses, the reactions begin about 250°C and is completed below 600°C, the reaction peak in the first sample S-glass is broader and not as great as with the second S-glass. The broadest of the peaks in the first S-glass, the difference in peak height, and differences in the effectiveness of either acetone or aqua regia in removing the coating indicate that the original coating on these two S-glasses are considerably different in composition.

3. Thermogravimetric Analysis

Comparison of the scanning electron micrographs and DTA data from the S-glass of the two principal samples studied show a difference in the composition and amount of the coupling agent present on the as-received fibers. In an effort to verify this information, thermogravimetric analysis (TGA) was employed. In this analysis, a sample is continuously weighed over a range of temperatures. The results are obtained in terms of percent weight change of the original sample. Samples between 12 and 20 mg. were burned in air at a programmed rate of 20°C per minute from room temperature to 600°C . The same basic equipment was used for the TGA as with DTA.

Figure 44 shows the TGA results obtained from S-glass furnished by both sources in the as-received state and the annealed condition. All fibers were ground and were from the same batches used in the DTA investigation. In both cases, a loss in weight is observed with the as-received S-glass. The second glass begins to lose weight about 230°C and stabilizes about 460°C with a total weight loss of 1.125 percent. The first as-received S-glass starts to lose weight about 280°C and stabilizes at 510°C with a total weight loss of 0.625 percent. These results indicate that a thicker and heavier coating of a different composition is present on the second S-glass and confirms the microscopic and DTA results.

The TGA results obtained from the annealed S-glass are quite different from those of the as-received glass. In both cases, a total gain in weight is observed, approximately 0.713 percent and

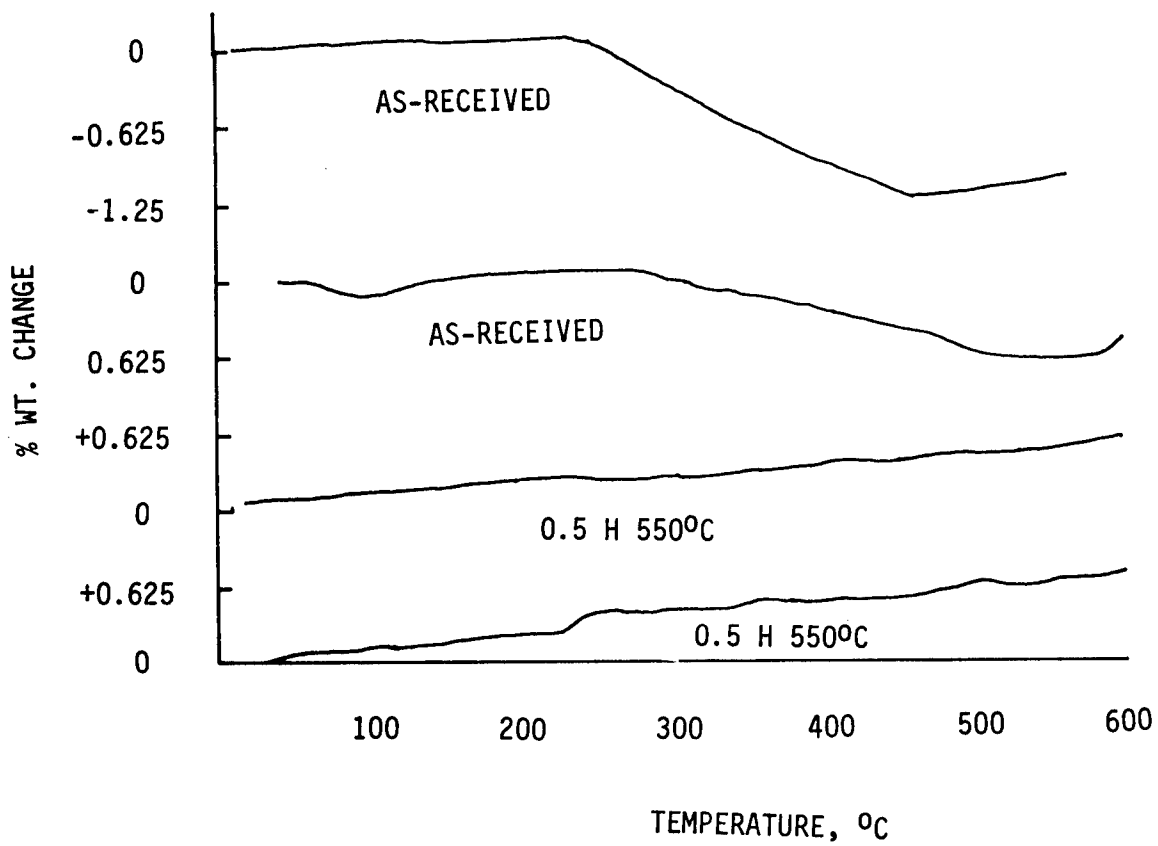


Figure 44. TGA curves of ground S-glass fibers showing percent weight change with temperature.

0.566 percent for first and second glasses, respectively. The exact cause for the weight gain is not known at the present time.

D. Light Scattering

The following experiment was believed to be possible and capable of producing meaningful results, although none of these results were realized. It is presented for the record as well as in the hopes that it may later provide a useful technique. The object is to measure the expected increase in light scattering due to the development of reaction products at the surface of the glass in the composite.

The method involves the use of strand-tensile samples with flat sides to allow the transmission of light with a minimum of scattering at the free surface. A principal objective is to be able to make such a study in samples that are to be used directly for evaluation of mechanical properties.

Samples were prepared in the same manner as described above for the standard strand-tensile sample specimen with the addition of two waxed, glass plates clamped across the central portion of the samples. Glass slides were given a thin coating of a silicone vacuum grease as a parting agent and were clamped using alligator clips. The result was samples with smooth parallel faces that caused negligible optical interference and allowed microscopic examination of the glass filaments embedded within the epoxy matrix. This shaping of a section of the sample produced no pronounced effect on mechanical properties, and had the optical scattering technique shown promise,

the flat-sided sample configuration would have been adopted for a large proportion of the samples tested.

As a preliminary experiment, several of the above samples were cut across in the center of the flattened region, and one-half of each of these samples was immersed in hot water for approximately one hour. These samples became visibly darkened, and the sets of as-fabricated and boiled samples were taken for optical examination. Both optical microscopy and light scattering results proved to be negative with no measurable differences between the samples in the two sets. Despite this evaluation, it is believed that the technique has merit and could lead to useful results with proper equipment involving a collimated source and precision optical detector. This required more time than could be justified for the objectives of this research. Therefore, this investigation was not pursued further.

E. Strand Tensile Test

1. Sample Preparation

ASTM Standard Procedure D-2343 includes a sample description of a composite sample meeting the needs for this research. This sample has a large proportion of glass in its constitution. Figure 45 is an outline of the equipment and steps involved in making the strand tensile sample based on this ASTM recommendation. The equipment is operated by hand. The spool of glass roving is placed on a pivot tilted at a convenient angle; the roving is fed through a pair of felt wipers that serve to provide back tension, over an idler pulley immersed in the epoxy mixture by means of a coating wheel,

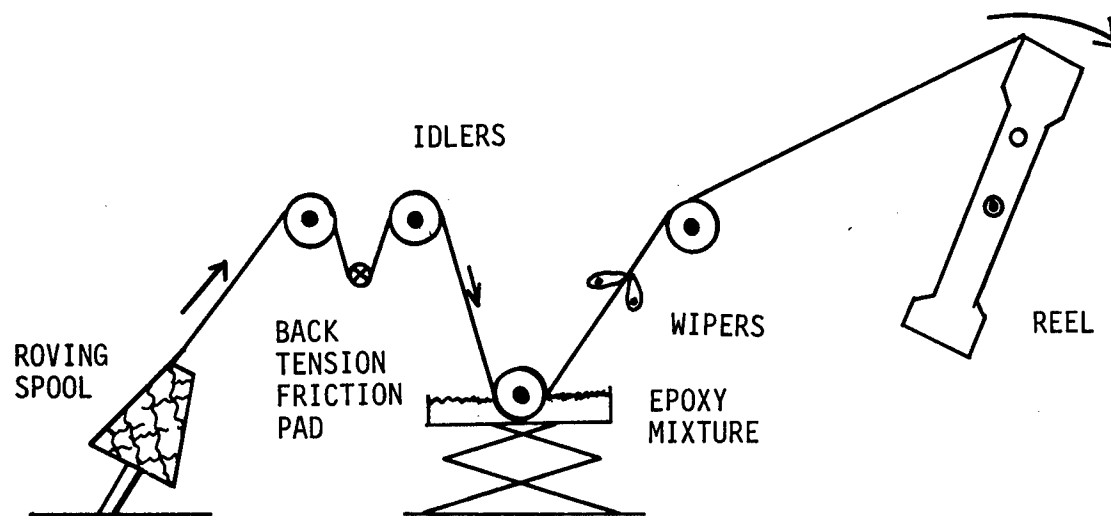


Figure 45. Strand tensile sample fabrication.

then the coated roving is passed through a pair of felt wipers to remove the excess epoxy, and is wound on a wooden reel. The depth of immersion is controlled by the position of the immersion cup on an adjustable laboratory stand and, when necessary, the supply of epoxy mixture is replenished with a brief interruption of the winding process. This equipment is set up on a chemical bench equipped with a glass rack. The surface of the bench and all equipment is liberally coated with paper and aluminum foil to guard against permanent spoilage by dripping epoxy mixture. Masking tape is used liberally to control the roving and to attach the roving to the wooden reel. When the roving is to be cut, it is found convenient to first tape the roving and cut through both the roving and the masking tape with shears.

The wooden reel, see Figure 46, made from common fir lumber in 2 x 2 cross-sections, is prepared by cutting two sides by bandsaw so that most of the coated samples will not be in contact with the reel, by bandsawing the slots on the end to separate the individual strands, and by drilling two holes--one for the pivot and one to facilitate winding and hanging in the curing oven. It was found to be necessary to prebake the reels in the curing oven for several hours prior to use because there is an initial shrinkage on curing which results in bowing of the samples.

The epoxy system used is Epon 828/D which is a commonly used structural epoxy. The epoxy and the curing agent are both degassed in a vacuum desiccator for several days at a pressure of a fraction

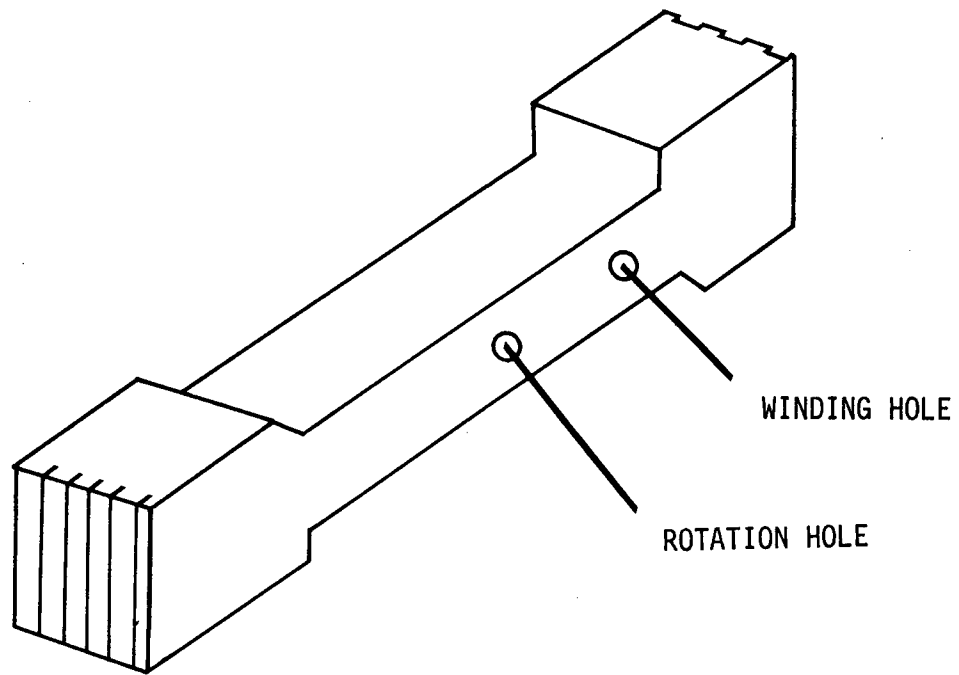


Figure 46. Wooden reel for strand tensile sample fabrication.

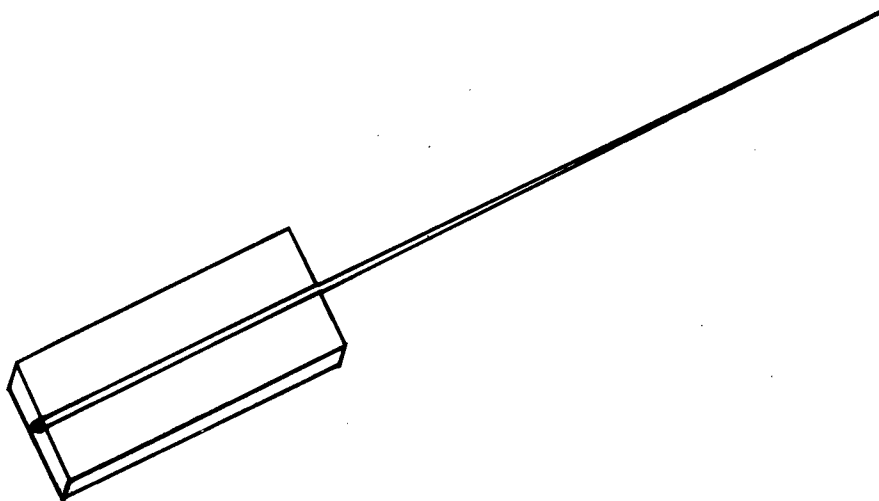


Figure 47. Grip end detail of strand tensile sample.

of a millimeter of mercury. This is found to eliminate porosity due to the release of gas bubbles. After winding, the reel is hung in the curing oven and cured for two hours at 200°F. The resulting samples have a uniform cross section and a smooth, but rippled surface.

After curing, the samples are cut from the reel. There is no problem with separation of the epoxy from the wooden reel. Any remaining epoxy is cleaned out with a bandsaw prior to curing an additional batch.

2. Testing

The composite samples are bonded into slotted aluminum blocks as shown in Figure 47. The blocks are machined so that the slots lie symmetrically along the center lines and are of uniform depth for both blocks. The two blocks are positioned at a controlled separation to define the gage-length of the sample, and an epoxy mixture that will cure at room temperature is used so that the properties of the sample will not be altered. No extensive testing has been done with these samples because no degradation experiments were begun during this period for reasons explained later. However, critical tests were performed with several of these samples to insure their applicability. It is found that the test is reliable if the end blocks are bonded over a length of one and one-half inches, and if the epoxy does not cover the top surface. If it covers the top surface, it will be shattered by the pressure grips used in the testing machine, and the end of the sample will usually slide out of the grips rather than being able to test the strand sample to the breaking point.

Also, it is found desirable to provide a positive means to prevent the blocks from sliding out of the grips. Pressure grips are not completely reliable in this type of testing. The features of the stress-strain curve are essentially linear, elastic deformation, with possibly some non-linearity close to the breaking point and then a relatively abrupt break. Figure 48 is a typical load-elongation curve from one of these samples.

F. Degradation and Chemical Analysis

The principal factor in the degradation of glass reinforced plastics was found in the earlier experiments and in the literature to be due to the reaction between water and the glass filaments in the composite. (24, 25) The action of water on the glass filaments would not only affect the strength of the filament, but also the bonding between the filaments and the coupling agent. Any sub-microscopic and microscopic gaps produced in the process will aggravate the degradation by allowing water to penetrate and spread into the interface between glass filaments and the resin matrix.

The course of deterioration of the composite is thus visualized to consist of sequential changes in its chemical composition, physical aggregation, and mechanical strength.

This section reports the results obtained in the experimental determination of chemical degradation of S-glass and E-glass rovings by water. Also included are the results on the action of water on a composite prepared from S-glass rovings and Epon 828/D epoxy resin, and of weak ammonia solutions on S-glass rovings.

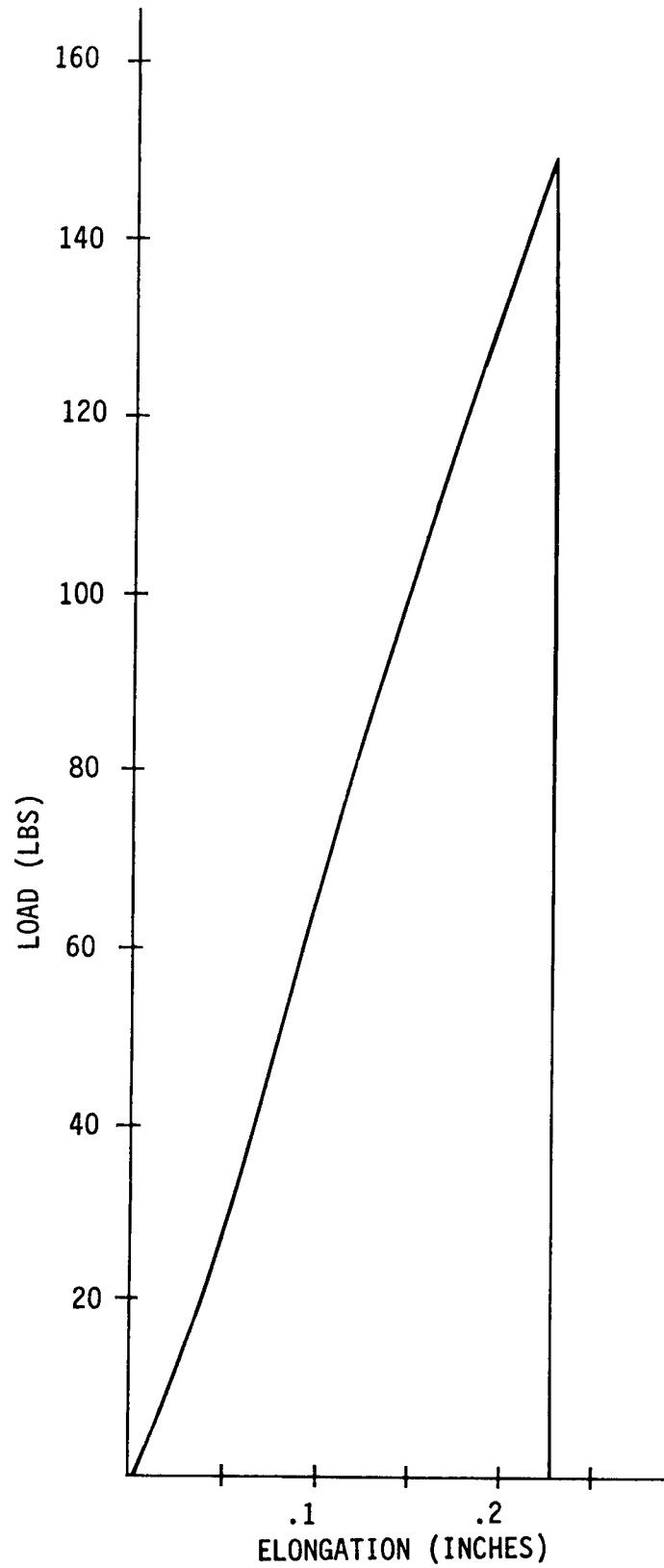


Figure 48. Typical load-elongation curve for strand tensile sample.

1. Degradation of S-Glass Rovings in Boiling Water

a. Effect of Time

The degradation of S-glass in the presence of moisture was studied by boiling Ferro Corporation's S-1014 S-glass rovings in water and determining the amount of magnesium in the liquid phase. Also, the pH change of the solution was followed. The low concentration of magnesium was determined by Perkin-Elmer Model 305 atomic absorption spectroscope.

One series of runs was made to study the effect of contact time on the extent of the reaction between water and the glass. The apparatus consisted of four sets of 500 ml. round-bottom Pyrex flasks heated by heating mantles and fitted with reflex condensers. The amounts of the rovings and water were, respectively, 9.5 grams and 100 ml. The results are summarized in Table III. The changes in magnesium concentration and pH with time are plotted in Figure 49.

It was noted that there was a band of solid deposits on the walls of each flask near the water-air interface. The deposits were scraped off from the walls and collected. They will be examined to determine their chemical and physical nature.

b. Effect of Amount of S-Glass Rovings

Another series of runs was made to study the effect of the amount of S-glass (hence the surface area). Different amounts of S-glass rovings were boiled with reflux for nine days in 100 ml. of distilled water in each of the 500 ml. Pyrex flasks as described earlier. The results are shown in Table IV and Figure 50.

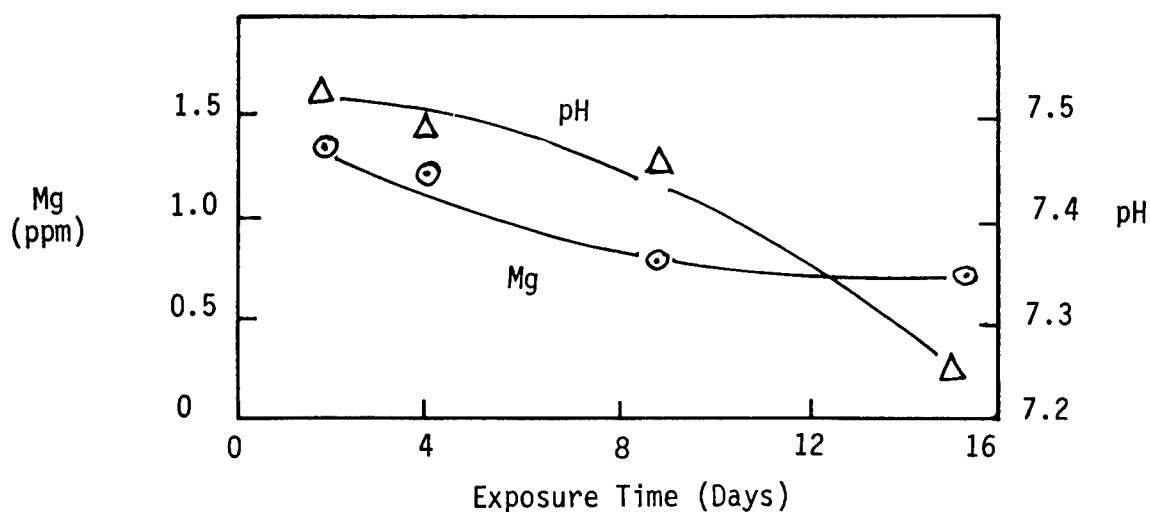


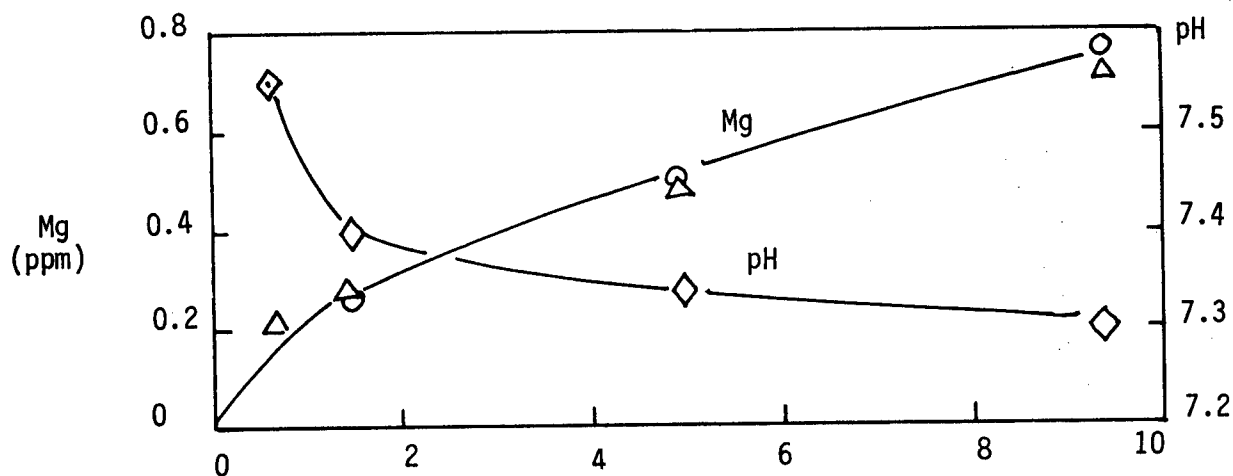
Figure 49. Effect of contact time on dissolution of magnesium from S-Glass in boiling water. 9.6 gm. S-G, 100 ml. water, in 500 ml. Pyrex flasks.

TABLE III

EFFECT OF TIME ON S-GLASS DISSOLUTION

(9.5 grams of S-glass rovings in 100 ml. boiling water)

Run No.	Time	Mg. in solution	pH
82	1 day 19 hr.	1.3 ppm.	7.52
84	4 days 0 hr.	1.20 ppm.	7.49
86	8 days 18 hr.	0.77 ppm.	7.45
88	15 days 0 hr.	0.70 ppm.	7.25



Grams of S-glass in 100 ml. boiling water

Figure 50. Amount of S-Glass on pH and Mg Dissolution. 100 ml. water in 500 ml. Pyrex flasks. For 9 days Duplicate analyses.

TABLE IV
EFFECT OF AMOUNT (SURFACE AREA) OF S-GLASS ROVINGS
(9 days in 100 ml. boiling water)

Run No.	Amount of S-glass rovings	Mg. in solution	pH
74	0.6434 gm.	0.200 ppm.	7.59
76	1.4084 gm.	0.275 ppm.	7.41
78	4.9063 gm.	0.500 ppm.	7.38
80	9.3388 gm.	0.775 ppm.	7.30

In both of these runs, it is evident from the pH readings that Pyrex glass (alkali borosilicates) and S-glass (aluminummagnesium silicates) interact, resulting in a solution with a pH value intermediate between those of the individual glasses.

The amount of magnesium in the liquid phase increases with the amount of S-glass present. The concentration of magnesium attained in both runs was 0.77 ppm. Since the final volume of the liquid phase was approximately 82 ml., the total dissolved magnesium amounts to 2.6×10^{-6} gm. atom. The removal of this amount should be sufficiently significant to affect the surface composition and structure of the S-glass filaments.

The aluminum concentration in the liquid phase determined by atomic absorption spectroscopy ranged between 2 and 3 ppm. which is higher than would be expected. This may be attributed to the interference exerted by the Pyrex (alkaline borosilicate) glass flask.

2. Degradation of S-Glass and E-Glass Rovings in Water at 40°C.

a. Effect of Amount of S-Glass Rovings

In view of the complications accompanying alkali borosilicate glass wares, it was felt that they should be judiciously avoided in investigations in which glass fibers are involved. Henceforth, most experiments were conducted in polypropylene or polyethylene containers.

One series of runs was made with 250 ml. polypropylene bottles, each containing 100 ml. distilled water but different amounts of S-glass rovings. The bottles were maintained in a constant temperature

bath at 40°C. for 9 days. The variations of pH and dissolved magnesium with amount of glass rovings are shown in Table V and Figure 51.

Figure 51 indicates that within a fixed time interval the amount of magnesium dissolved increases with the amount of S-glass rovings present. It also indicates that the time interval should be extended beyond the nine days covered in this series.

b. Effect of Time of Contact between Glass and Water at 40°C.

1. S-glass

Two series of runs were conducted in polypropylene bottles to determine the action of water on S-glass rovings at 40°C. The first series had approximately 10 grams of S-glass rovings in 100 ml. of distilled water and the second series had approximately 10 grams of the rovings in 150 ml. of distilled water. The amounts of magnesium, aluminum, and silicon in water were determined after different time intervals (up to 59 days). Atomic absorption spectroscopy was used for magnesium and aluminum analyses; the heteropoly blue colorimetric method was used for silicon concentration measurement. The results are summarized in Tables VI and VII.

Tables VI and VII signify the following points:

(1) The low concentration of Al_2O_3 is apparently attributable to its low solubility in water. The solubility of Al_2O_3 in water at 29°C. given in the literature is equivalent to 0.52 ppm. by weight of aluminum. (26)

(2) The solubility of MgO in water at 30°C. given in the literature is equivalent to 52 ppm. by weight of magnesium. (26)

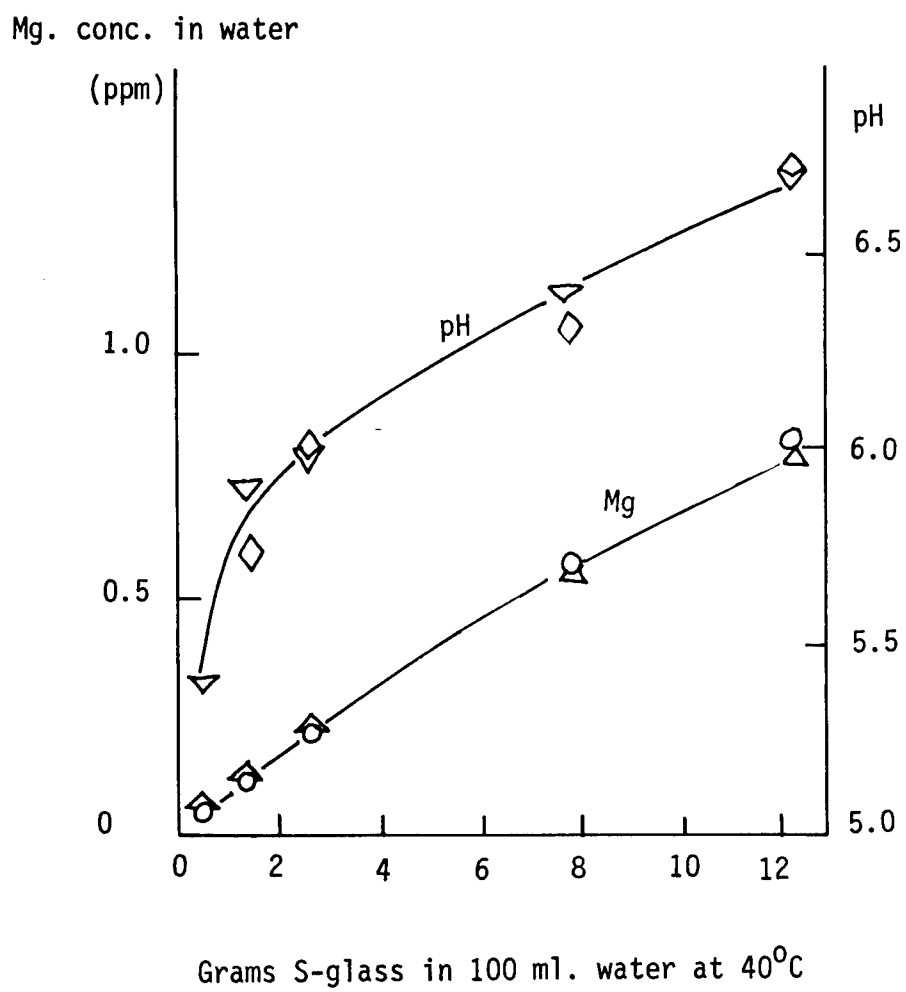


Figure 51. Degradation of S-glass in water at 40°C in Polypropylene bottles.

TABLE V
EFFECT OF AMOUNT OF S-GLASS ROVINGS
(9 days in 100 ml. water at 40°C.)

Run	S-Glass rovings (grams)	Analysis of Solution*			
		Mg	(ppm)	pH	
62	0.5896	0.054	0.075	5.20	5.42
64	1.3319	0.125	0.140	5.75	5.90
66	2.5520	0.215	0.225	5.98	5.99
68	7.7353	0.563	0.550	6.31	6.41
70	12.2944	0.802	0.765	6.74	6.69
72	0.0	0.0	0.0	5.30	5.20

* Concentrations of aluminum in all runs were no more than 0.2 ppm. The Perkin-Elmer Model 305 atomic absorption spectroscopy was not able to analyze aluminum at such low concentrations.

TABLE VI
DISSOLUTION OF S-GLASS INGREDIENTS IN WATER AT 40°C.
AFTER DIFFERENT TIME INTERVALS
(Water in each Polypropylene Bottle = 100 ml.)

Run	Amount of S-glass	Contact Time	Concentration in Water (ppm)* Mg	Si
102	10.06516 gm.	14.3 hr.	0.30	---
104	10.30634	42.5 hr.	0.39	3.55
106	9.92475	91.1 hr.	0.55	4.00
108	10.18098	232.6 hr.	0.87	4.05
110	9.95955	376.6 hr.	1.06	4.60
112	9.87234	646.3 hr.	1.34	5.12

* The concentrations of aluminum in all runs were no more than 0.2 ppm.

The Perkin-Elmer 305 atomic absorption spectroscope was not able to analyze aluminum at such low concentrations.

In one series of runs with S-glass made with water at approximately 90°C., the concentration of magnesium reached as high as 22 ppm. Clearly, it is possible to approach the solubility limit if contact between the glass rovings and water is sufficiently prolonged.

(3) The unexpectedly high concentration of silicon probably comes from decomposition, by water, of the silane coupling agent on the S-glass rovings.

The increase of magnesium concentration in water with increasing time is plotted in Figure 52 for the two series of runs.

The amount of magnesium in the solution in relation to the amount of S-glass is expected to be representable by an equation of the following form.

$$r = \frac{-dG}{dt} = kS^m (C_s - C)^n \quad (1)$$

r is the rate of degradation of S-glass, k rate constant for the system, S surface area of S-glass, C_s saturation concentration, C concentration time t , and m and n represent the reaction orders with respect to the surface and concentration driving force, respectively. dG is the change in amount of S-glass.

Equation 1 may be rearranged and integrated.

$$\int_{G_0}^G -dG = \int_{t_0}^t kS^m (C_s - C)^n dt \quad (2)$$

G_0 and G are, respectively, amounts of S-glass at initial time t_0 and time t . The applicability of Equation 2 is to be verified when additional results become available.

ii. E-glass

The action of water on E-glass rovings (Ferro Corporation #1136A) was investigated in the same manner as on S-glass rovings. Approximately 10 grams of E-glass rovings was in contact with 150 ml. of water in polypropylene bottles maintained at 40°C. in a constant-temperature water bath. The concentrations of magnesium, aluminum, and silicon in the water were determined after different time intervals. The results are given in Table VIII. The variation of the amount of magnesium in water with time is shown in Figure 53.

Based on the results given in Tables VI - VIII and Figures 52 - 53, the following points may be drawn.

(1) With both S-glass and E-glass rovings, the magnesium concentration increases rapidly at first, and then slowly, with time. The slow increase is possibly related to the diffusion of magnesium within the glass structure to the filament surface. Runs will be made at several temperatures in order to elucidate this point.

(2) The high solubility of MgO in water makes it more readily removable by moisture from the glass rovings. The loss of MgO would probably affect detrimentally the structure and strength of the glass filaments.

(3) The high concentration of dissolved silicon indicates ready decomposition of the silane coupling agent by water. The removal of the coupling agent presumably affects the bonding between the glass filaments and the resin matrix in a composite.

TABLE VIII
DISSOLUTION OF E-GLASS INGREDIENTS IN WATER AT 40°C.
AFTER DIFFERENT TIME INTERVALS
(Water in each polypropylene bottle = 150 ml.)

Run	E-Glass (grams)	Contact Time (hours)	Concentration of Mg (ppm)	Ingredients* Si (ppm)
131	9.7234	116	1.40	3.80
132	9.9390	234	1.68	4.25
133	10.3928	587	2.00	3.80
134	10.3912	950	2.05	5.70
135	9.6328	1244	2.20	----
136	9.8014	1416	2.47	----

* The concentrations of aluminum in all runs were no more than 0.2 ppm.

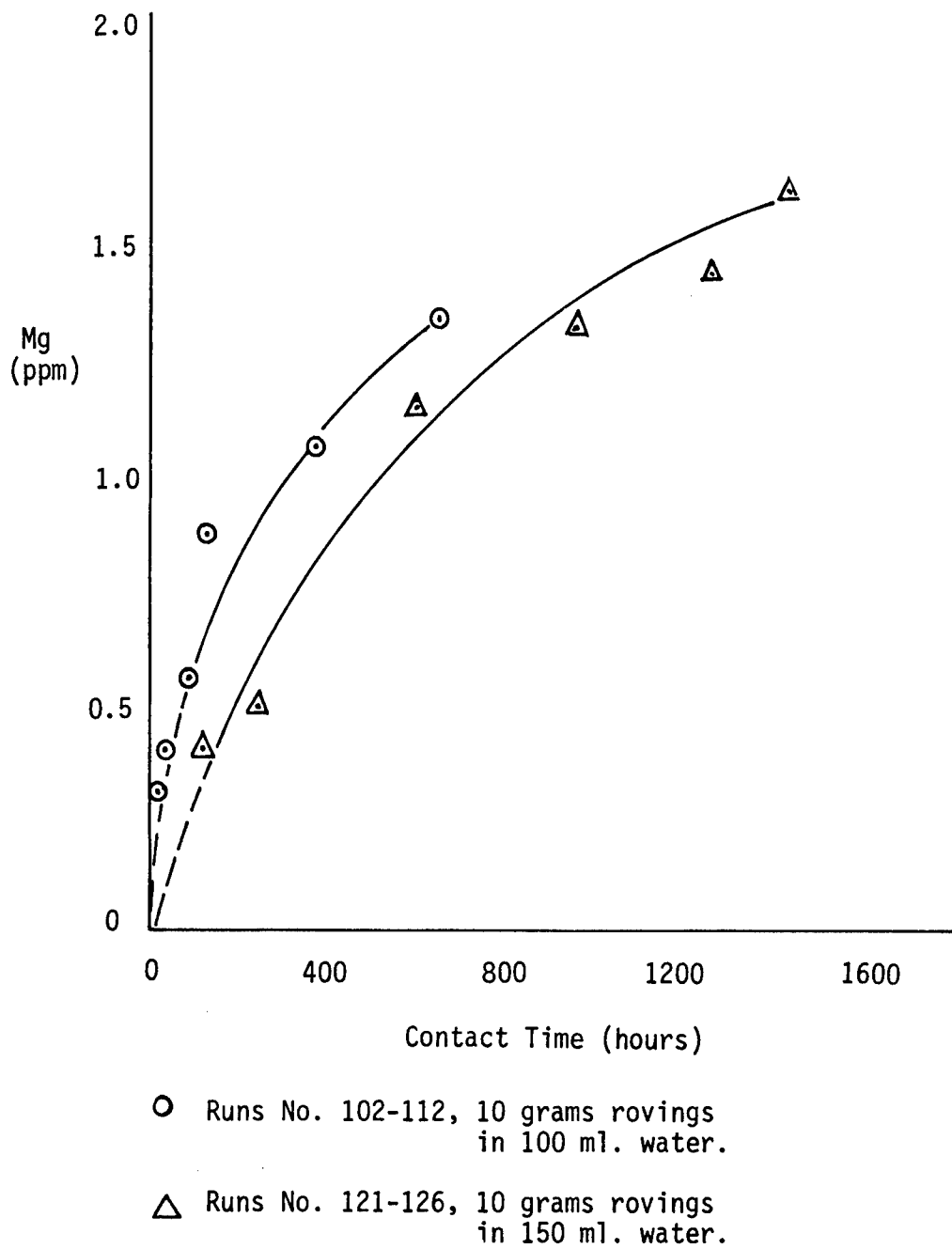


Figure 52. Magnesium concentration in water after different time intervals at 40°C. for S-glass rovings.

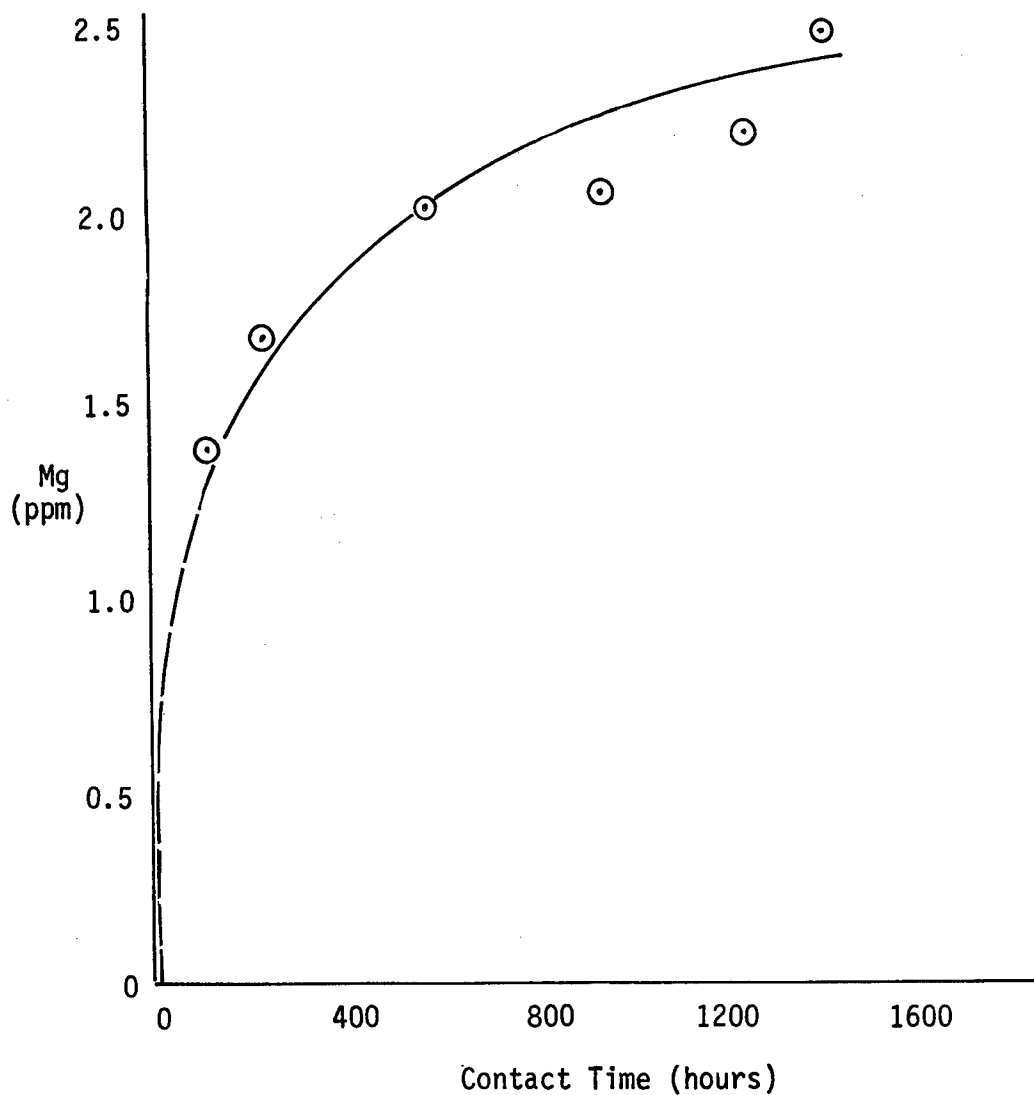


Figure 53. Magnesium concentration in water after different time intervals at 40°C. for E-glass rovings 10 gms. rovings in 150 ml. water.

TABLE VII
DISSOLUTION OF S-GLASS INGREDIENTS IN WATER AT 40°C.
AFTER DIFFERENT TIME INTERVALS
(Water in each polypropylene bottle = 150 ml.)

Run	S-glass (grams)	Contact Time (hours)	Concentration of Ingredients*	
			Mg (ppm)	Si (ppm)
121	9.9836	116	0.40	0.75
122	9.8148	234	0.50	0.75
123	10.3466	587	1.15	1.61
124	10.0108	950	1.33	1.95
125	9.6245	1244	1.44	2.1
126	10.3369	1416	1.62	2.42

* The concentrations of aluminum in all runs were no more than 0.2 ppm.

(4) S-glass has a higher MgO content than E-glass has (10 weight % versus 4.5 weight %), but under comparable experimental conditions the water in contact with E-glass rovings contains slightly more magnesium than that with S-glass rovings. As the compositions of S-glass and E-glass are quite different, some of the ingredients in E-glass, which are not present in S-glass, apparently tend to enhance the dissolution of MgO in water.

3. Degradation of S-Glass Composites

This series of runs was made to investigate the dissolution in water of a S-glass composite as compared with that reported earlier for the bare rovings. The composite was prepared with Ferro Corporation's S-1014 S-glass rovings and Epon 828/D epoxy resin. The nine-inch long composite rods initially obtained were cut to one-inch strands. Sixty of these strands were washed with 10 ml. distilled water before being transferred to an 8-oz. wide mouth polypropylene bottle. Sixty strands weighed an average of approximately 2.45 grams. They were immersed in 60 ml. of water in the polypropylene bottle maintained at 40°C. in a water bath thermostat.

The water in different bottles was decanted after different time intervals (ranging between 3 to 49 days) and analyzed for its Al, Mg, and Si contents and pH. Atomic absorption spectroscopy was used for Al and Mg determinations Si colorimetric. The results are summarized in the Table IX.

This series cannot be strictly compared with that for the bare S-glass rovings reported earlier, because the amounts of water

TABLE IX
 DEGRADATION OF S-GLASS COMPOSITE* IN WATER AT 40°C.
 60 ONE-INCH STRANDS (2.45 GRAMS) IN 60 ML. OF WATER

Run	Contact time (hours)	Al (ppm)	Mg (ppm)	Si (ppm)	Analysis of Water Solution pH
114	67	< 0.1	0.05	2.51	**
115	168	< 0.1	0.02	3.35	6.30
116	408	< 0.1	0.02	2.51	5.70
117	666	< 0.1	0.02	2.54	4.75
118	1172	**	0.06	2.54	4.70
119	1436		0.05	2.54	

* Ferro 1014 S-glass rovings and Epon 828D epoxy resin.

** Supply of solution ran out.

and glass rovings used in these two series were not corresponding. However, the data indicate, as expected, that the dissolution of magnesium was far smaller due to the smaller surface exposure by the composite.

The pH of the solutions shows a decreasing trend with increasing time of exposure. Apparently, some ingredients in the epoxy resin formulation contribute to the increase in acidity. This is in contrast with the case of bare S-glass rovings reported earlier, in which the trend was for increasing pH with increasing time of exposure in water.

4. Degradation of S-Glass Rovings in Weak Ammonia Solutions

Runs were made to determine the presence of a small amount of ammonia in water on the rate of dissolution of S-glass rovings. The initial solutions of ammonia ranged between 0.0404 M and 0.0000808 M. The contact time between the S-glass rovings and the ammonia solutions consisted of 13 days at 40°C and 14 days at 24°C. The final solutions were analyzed for pH, aluminum and magnesium, the latter by atomic absorption spectroscopy. The results are summarized in Table X.

It may be noted from Table X that the concentration of aluminum (or Al_2O_3) reached around 2 ppm. in the weak ammonia solutions, in which the pH was in the alkaline region. This is in contrast with the low aluminum concentration (less than 0.2 ppm.) when water was used.

The results plotted as Figure 54 shows that the amounts of magnesium and aluminium dissolved increases with the pH value of

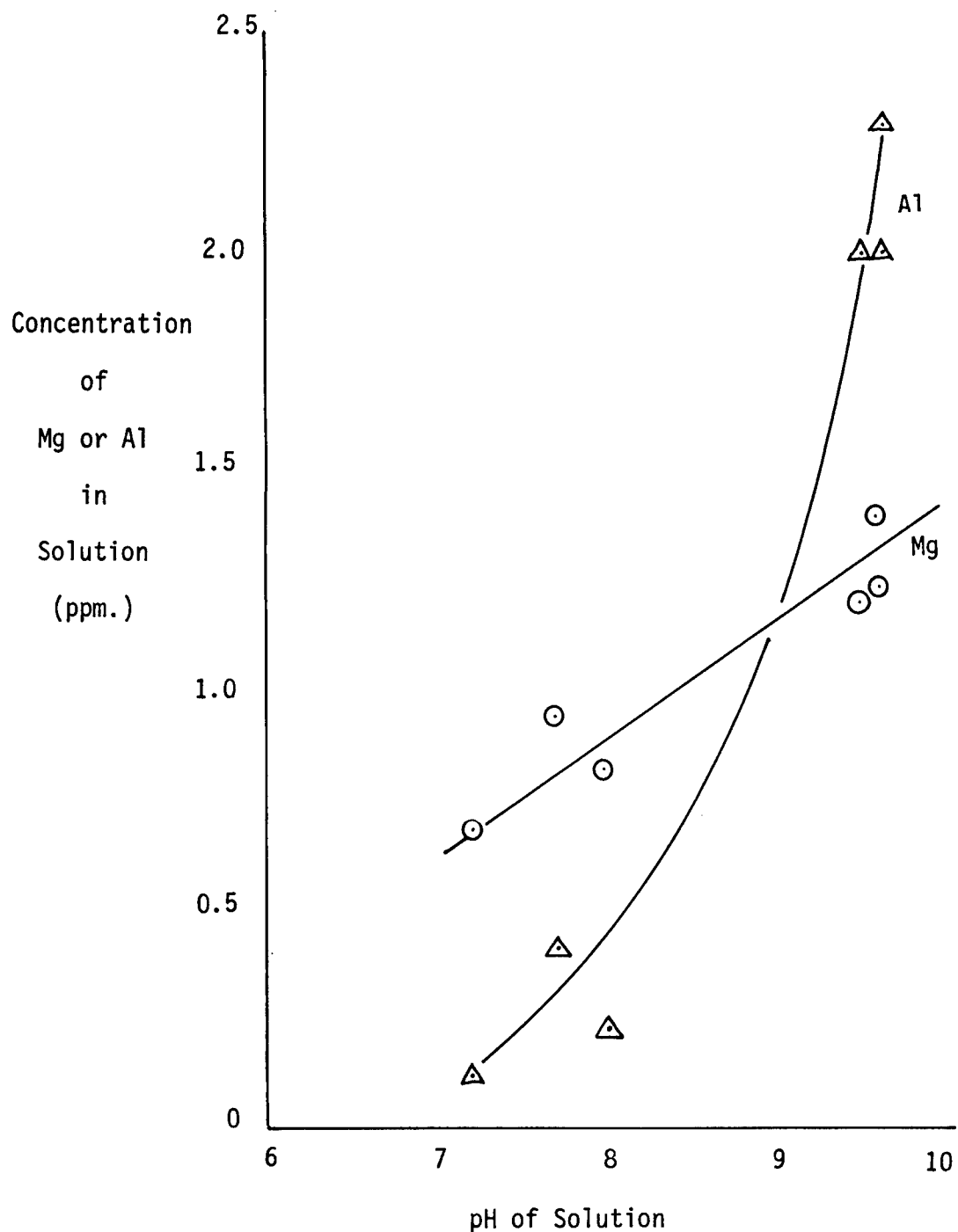


Figure 54. Degradation of S-glass roving in weak ammonia solutions 5.5 grams of roving in 100 cc. solution ammonia solution concentration: 0.0404M - 0.000080M 2.5.

TABLE X
 DEGRADATION OF S-GLASS ROVINGS IN WEAK AMMONIA SOLUTIONS*
 FERRO CORPORATION'S S-GLASS (S-1014) ROVINGS
 (Amount of ammonia solution in each bottle = 100 ml.)

Run	Amount S-glass (grams)	Initial conc. of ammonia (molar)	Magnesium in solution (ppm.)	Aluminum in solution (ppm.)	pH
90	5.770	0.0404	1.21	2.0	9.50
92	5.530	0.00808	1.25	2.0	9.61
94	5.417	0.00404	1.41	2.3	9.58
96	5.907	0.000808	0.825	0.22	7.98
98	5.506	0.000404	0.950	0.41	7.70
100	5.709	0.0000808	0.690	0.12	7.21

* Contact time: 13 days at 40°C. and 14 days at 24°C.

the solution. This conforms with the information reported in the literature for Pyrex glass that the rate of attack on the borosilicate glass by aqueous alkaline solutions increases rapidly with increasing pH when the latter exceeds 9.0. (23)

Ammonia and amines are possible products when amino silanes and amino curing agents used in glass reinforced plastics finishing and formulations undergo decomposition in the presence of moisture, microorganisms, and other factors. Deterioration of glass reinforced plastics by this sequence of processes is conceivable. Further work is needed to investigate if this is the case, and the means to prevent it.

5. Summary and Conclusions

a. In the investigation of degradation of glass filament reinforced plastics, use of glass wares, including Pyrex, should be judiciously minimized to avoid interference between the glasses, and the obscuring of chemical analyses.

b. In this research, polyethylene and polypropylene, instead of Pyrex, containers were used, with the temperature mostly at 40°C. The low experimental temperature probably yields conservative but more representative results.

c. The dissolution of aluminum from S-glass rovings in water after immersion for more than 50 days at 40°C. amounted to no more than 0.1 or 0.2 ppm., the detection limit of the present atomic absorption spectroscope. The dissolution of magnesium under the same conditions, however, amounted to more than 1.6 ppm. and increased with increasing contact time. Apparently, the amounts

of Mg and Al found in the liquid phase are directly related to the respective solubility of MgO and Al_2O_3 in water.

d. Under the same conditions, the water in contact with E-glass rovings for 59 days contained 2.5 ppm. Mg versus 1.6 ppm. with S-glass rovings, although the magnesium content as MgO in the former is less than one-half in the latter (4.5 weight % vs. 10 weight %).

e. The dissolution of aluminum was considerably enhanced by high pH values in solution as the case with weak ammonia solutions. This is in congruence with the literature information that the attacking rate on Pyrex glass by alkaline solutions increased rapidly at pH values greater than 9.0. The effect of pH on the dissolution of magnesium was not appreciable.

f. The concentrations of silicon in water in contact with S-glass and E-glass rovings were found to be more than 4 ppm., far greater than the solubility of silicon dioxide of any form. It is suspected that the silicon in the liquid phase comes from the silane coupling agent on the rovings. The results with S-glass and E-glass powders should establish whether the glass or silane coupling agent is the silicon source.

g. Based on the results obtained, it becomes increasingly convincing that Mg (or MgO) is a weak factor in the structure of S-glass and E-glass on exposure in water.

III. RESULTS AND DISCUSSION

A. Objectives and Summary of Results

At the start of this period of research the fact of degradation was well documented and recognized but the nature of the process or processes was unknown. The philosophy in the research was to determine the reactivities of the principal constituents in the system with the objective of relating these behaviors to that of the composite. [Work conducted in this laboratory during a previous contract showed that the degradation of the filaments had a characteristic time dependency similar to that of the composite. During this period, direct chemical analyses were made on the glass and on the reaction products after exposure to water by immersion and by exposure to high humidity atmosphere. Degradation is the direct result of a reaction between water molecules and the chemical bonds between silicon and oxygen in the glass. Glass fibers lose their strength rapidly as do the composites, although the change in strength of the individual filaments is found to be much more rapid and pronounced than that of the composites. The polymer matrix effectively reduces the rate of diffusion of the water molecules to the glass surface. It does not, however, block reaction.

Earlier research showed that the action of water on the mechanical properties of the individual glass fibers has a stabilizing effect and can result in a recovery of mechanical properties after the initial degradation. This is an indication that the glass surface contains a variety of structural features with a spectrum of reactivities. First reactions apparently reveal stress concentrating

surface features and subsequent reactions tend to affect the general surface leaving it in a smoother and more stable condition.

Direct studies were performed to attempt to measure the heat released by the reaction. Initial, promising results using the differential scanning calorimeter showed promise but later review of the experiment showed that the principal affect was that of a thermal imbalance caused when the moist atmosphere was added to the system. It is felt, however, that the reaction must occur within the few minutes that are known to result in a loss of mechanical properties and must, therefore, be traceable with equipment of adequate sensitivity.

The chemical analysis has indicated that magnesium ions are removed at a faster rate from the glass surface than either aluminum or silicon ions. This strongly indicates that the magnesium ions incorporated in the silica structure may be active in the degradation process. Such components as magnesium and aluminum have an affect of modifying both the chemical reactivity in the region of their presence as well as in modifying the basic phase structure in the glass. In a fixed composition glass such as the S-glass studied in this research this should be a constant factor except that chemical segregation is known to occur and will have an effect on reaction rate. An additional factor not studied during this research period but planned for a continuing period is that of cyclic stress. Glasses are known to be sensitive to stress corrosion and the associated changes in spacing between structural branches in the glass will affect the reactivity.

The possible approaches to the stabilization of the glass includes surface passivation with a non-reactive layer of another glass; surface passivation of the glass by ion exchange to render the surface hydrophobic; stabilization of magnesium in the glass through chemical and physical treatment; the development of a dense, protective silane, organic, or other coating on each glass filament; or the development of a dense protective polymer for the matrix. There is evidence through the work reported in the scientific literature by other investigators that each of these proposed methods is possible and should be further investigated; however, reports of stabilization experiments have not been published.)

B. Stabilization Program

The interaction between water and glass includes several stages such as simple adsorption involving the secondary chemical bonding of water molecules to the surface of the glass. This process may occur with different characteristics at different local regions on the glass, depending upon the local structure and presence of foreign ions. A second type of interaction is direct reaction in which the silicon-oxygen linkage is broken and by which fragments of silicate are released. In solution these may be carried away. In the composite, they are entrapped at the interface.

Applied research in pursuit of a solution to this degradation involves activity at three levels. These are outlined in Figure 55. Specific investigations into methods to protect or passivate the glass surface are the first level. The effect of water treatment

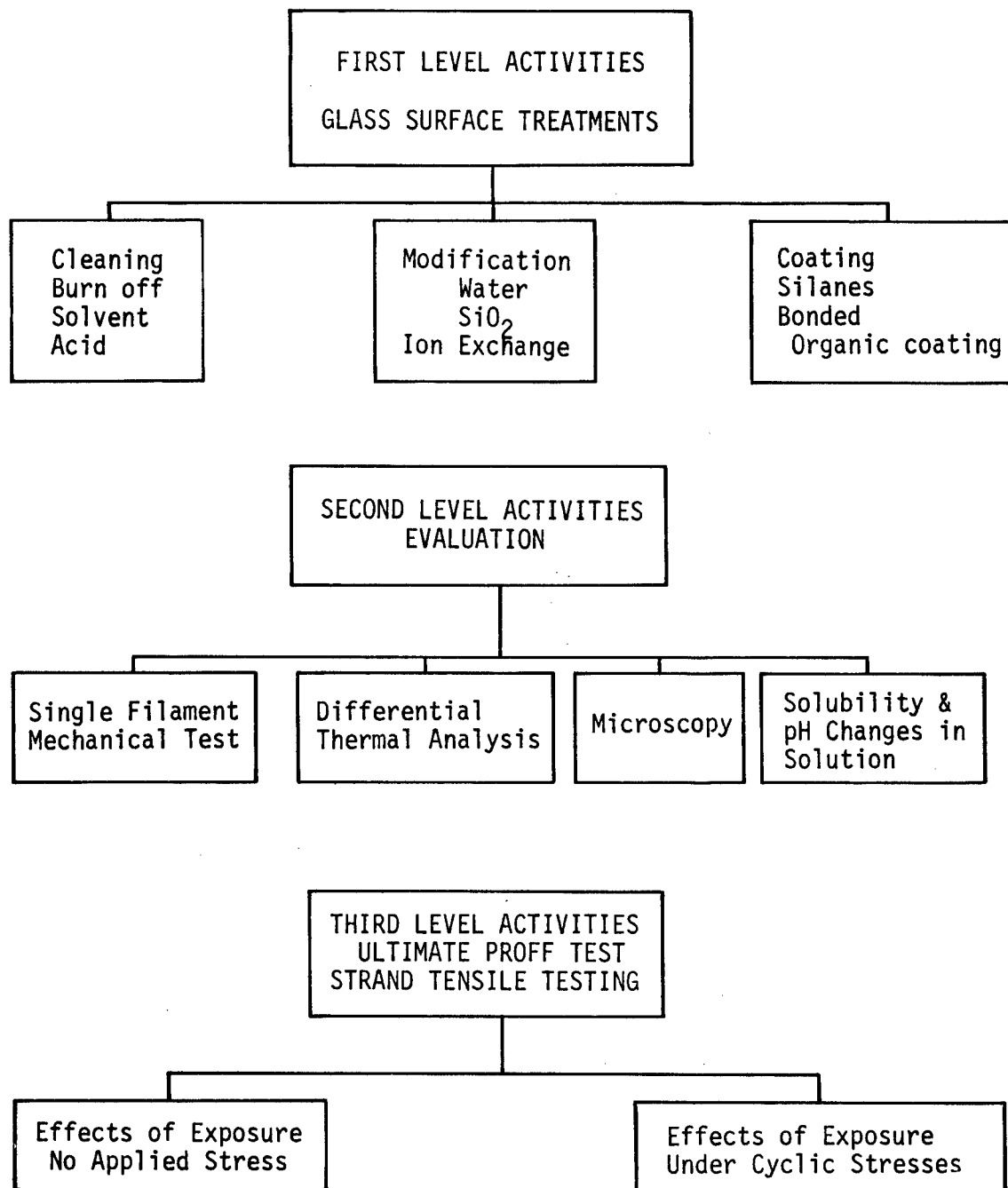


Figure 55. The heirarchy of activities to find a solution to the degradation of S-glass - epoxy composites by water.

on the filaments and composites was a study at this level.

Methods to evaluate the treatments conducted at the first level comprise the second level of investigation. The development of the direct mechanical test procedure for the individual filaments as well as the studies of magnesium ion concentration change and pH change in solution are examples of this level of activity. The most recent research at this level is the application of differential scanning calorimetry to the direct analysis of the reaction between glass and water. Passivated surfaces directly alter the parameters of this reaction.

The third level of investigation is into the resulting composite properties following a glass surface treatment selected in the other two levels of investigation. The primary emphasis must be placed at the first two levels following the description above. There is a possibility of finding a method to reduce reactivity.

1. First Level Activities

Water treatment showed a pronounced effect in reducing the scatter of mechanical properties. The first effect of the water is to remove reactive molecular groups from the surface of the glass, thus creating relatively rough, stress-concentrating features. Continued exposure to water smooths the surface around these defects, reducing the stress concentration effect and leaving a surface with a lower defect concentration. Experiments with water treatment of individual glass filaments showed a recovery of filament strength with continued exposure. It is believed that with special processing techniques to avoid damage to the glass

filaments in the bare condition during treatment that the composite properties may be retained at the maximum strength level.

Bascom and others reported on the benefits of forming close packed chemical films on the surface of the glass. The proprietary finishes currently used are not deposited under conditions to promote the formation of a densely packed layer. (20)

There is a possibility that specific chemical treatment, probably involving ion exchange, may serve to stabilize the glass surface chemically and mechanically. A number of these will be investigated. This is analogous to the reduction of tooth decay by using fluoride-containing cleansers.

The exact nature of the bonding between either the silane finish or the epoxy and the glass surface is not yet established in every case. There is, therefore, a need to perform a direct chemical bonding experiment by the method of Hamann. (21) He employs successive chemical treatments to replace surface hydroxyls with bromides and then to replace the bromides with organic groups by reactions with lithium salts of those organic groups.

The above are examples of surface treatment techniques that have either been tried or are being considered or pursued.

2. Second Level Activities

The most direct evaluation of the results of any surface treatment are made without formulating a composite with epoxy resin. The most direct evaluation procedure used was the mechanical testing of the individual glass filaments. This showed that the degradation characteristics of the filaments paralleled that of the composites.

a. Differential Thermal Analysis (DTA)

The use of DTA methods is a means of studying the reaction of glass with water. DTA of water pre-treated glass will produce results similar to those obtained by Landau (22) et al for a catalyst surface (See Figure 56.)

Differential Thermal Analysis can be used to characterize the nature of coatings and possibly to follow the basic degradation reaction although experiments relative to this last have failed to date.

b. Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy of S-glass fibers has been utilized to determine the effectiveness of hot dilute solutions of sulfuric acid, hydrochloric acid and chromic acid in removing the sizing from the as-received glass. These acid treatments may eliminate heat treating the glass at 550°C. Burning-off of the sizing may alter the surface of the glass. The effect of treating the glass with acids to remove the sizing may also be studied using DTA.

The SEM may be used to investigate the effects of water treatment on the surface of glass powders. After various treatments of powdered glass in room temperature or boiling water, SEM may be utilized to determine the effect of water on the size and rounding of asperities of the glass particles. The effect of various sizings on the water treatments will also be investigated. The necessary resolution for this is not as great as required for the surface study of fibers. The results of the SEM study can be

correlated with the DTA data.

c. Effect of Water on S-Glass at Ambient Temperature

The effect of water on S-glass has been studied by determining the amounts of the atomic components, aluminum, magnesium and silicon, dissolved in the water. This series of runs was conducted with S-glass rovings contained in polypropylene bottles containing 100 ml. of distilled water and maintained at 40°C in a constant-temperature bath. It is seen that the amounts dissolved in water are in variance with the composition of S-glass. The following points may be drawn:

i. The ingredients dissolve incongruently, as expected, from the S-glass solid phase.

ii. The low concentration of Al_2O_3 may be attributed to its low solubility. The solubility of Al_2O_3 in water at 29°C given in the literature is equivalent to 0.52 ppm by weight of Al.

iii. The dissolution of MgO increases slowly with time. The rate of increase of Mg concentration in the solution is probably controlled by the rate of diffusion of Mg within the S-glass filaments to the solid-phase surface. The solubility of MgO in water at 30°C given in the literature is equivalent to 52 ppm by weight of Mg. In one series of runs with S-glass in water maintained at approximately 90°C, the concentration of Mg did reach as high as 22 ppm. Clearly, it is possible to approach the solubility limit of the ingredients if contact between the glass and water is sufficiently prolonged.

iv. The unexpectedly high concentration of SiO_2 probably comes from decomposition, by water, of silane coupling agent on the S-glass rovings.

In the foregoing, two points of particular interest and concern should be brought out here.

a. The high solubility of MgO in water makes it more readily removable by moisture from S-glass. The loss of MgO is probably detrimental to the structure and strength of the S-glass filaments.

b. The high concentration of dissolved Si indicates ready decomposition of silane by water. The elimination of the coupling agent would presumably weaken the bonding between the S-glass filaments and the resin matrix in a composite.

3. Third Level Activities

Following selection and evaluation of a specific surface treatment, the effects of that treatment on composite degradation characteristics must be determined. The degradation characteristics for S-glass-epoxy composites was determined using samples in the strand tensile sample configuration. The results were found to be consistent with the work of others.

IV. RECOMMENDATIONS FOR FURTHER WORK

The results of the research performed under this contract are in agreement with the results found by other investigators in that the glass is identified as a principal reactive component in the glass reinforced epoxy composite structural materials system. It was also found that the magnesium component in the glass phase is active in the degradation process because its concentration was found to increase continuously throughout the experiments.

It is recommended that further work be directed towards stabilization of the glass against reaction with water. This research should include consideration of the use of different glass compositions and ways to produce a composite glass with a non-reactive surface layer and a stronger and less expensive core. There have been many investigations regarding the structure and properties of individual glass formulations, but relatively little work has been reported on methods to stabilize the glass against reaction with water. This research is imperative.

It is felt that the most productive research will be to place the primary emphasis on the design and control of finishes and methods of application of the finish materials. Scanning calorimetry and other analytical procedures have shown the variability of the finish that is supplied with the rovings. Chemical analyses showed the possibility that the coupling agent is actively reacting with water. This reaction would be sufficient to cause a degradation in composite properties. The use of glass filaments that

are supplied with proprietary finish materials is a very dangerous practice because the glass surface is the most sensitive region in the system. Any slight alteration of composition of the structural components in the composite in this region will have a pronounced, undesirable, effect on composite mechanical properties.

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